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Supercritical Carbon Dioxide Treatment of Oil Contaminated Drill Cuttings

by

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ABSTRACT

Supercritical carbon dioxide (SC CO_2) treatment of oil contaminated drill cuttings is a promising new technology. In this work, supercritical carbon dioxide was successfully used to extract oil from raw centrifuge-underflow oil-based mud (OBM) drill cuttings obtained from active drilling sites. Extraction experiments were conducted at several conditions of temperature and pressure ranging from 35 to 60°C and 8.3 to 17.2 MPa, respectively, with a 45-minute single cycle extraction and magnetic stir bar mixing. The raw and extracted cuttings' petroleum hydrocarbon (C_{10}-C_{32}) contents were determined by gas chromatography/flame ionization detection (GC/FID). An optimal single cycle extraction efficiency of 90% was obtained at 60°C and 12.4 MPa, reducing the cuttings petroleum hydrocarbon content from 17.19% to 1.76%. At the same conditions, 90-minute double cycle extraction increased the efficiency to 97%, reducing the cuttings petroleum hydrocarbon content to 0.55%. SC CO_2 recovers the expensive drilling mud oil, which can be reused in the drilling operation, while leaving "clean" and dry" cuttings.

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DEDICATION

In appreciation of the innumerable mercies, opportunities and love I have graciously enjoyed, this work is dedicated to the source of life and giver of all wisdom and strength, God almighty and my Lord and Savior, Jesus Christ.

Also dedicated to my dear wife Sola.

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CHAPTER 1 INTRODUCTION

Drilling for oil and gas involves the use of drilling fluids, primarily to remove rock fragments from the drilling well and transport them to the surface (USEPA 2000; CAPP 2001). Drilling fluids could be gas, foam or the more commonly used liquid-based fluids called drilling muds (used for approximately 93 percent of wells (API 1997)). The material removed from the drilling well is referred to as drilling waste, and therefore is composed of the drilling mud (liquid phase with additives) and drill cuttings (rocks). Most of the drilling mud is reused and the drill cuttings contaminated with some drilling mud must be treated and/or disposed off (AEUB 1996; USEPA 2000; CAPP 2001).

There are three general mud classifications: oil-based muds (OBMs), water-based muds (WBMs) and synthetic-based muds (SBMs) (USEPA 2000). OBMs are composed primarily of hydrocarbon diesel oil or mineral oil and additives, WBMs consist of a base of salt or fresh water containing additives, while SBMs have oil-like or synthetic base materials with additives (USEPA 2000; CAPP 2001). WBMs are not able to perform as well as OBMs in deep holes with high temperature conditions. OBMs are well suited for high temperature conditions as oil components have higher boiling points than water (USEPA 2000). SBMs generally perform better than WBMs, but less well than OBMs (USEPA 2000). In comparison with WBMs, OBMs also possess better lubricity, generate cuttings that are easier to remove, and create a smaller amount of drilling waste. The advantages of OBMs over WBMs and SBMs are even more crucial as it is predicted that OBMs will become more prominent as the industry trend is towards deeper wells (USEPA 2000).

Oil-contaminated drill cuttings are generally disposed of or treated by inerting, bioremediation, cleaning, or deep-well re-injection (USEPA 2000). Inerting consists of solidifying the drill cuttings so that the oil components are not leachable. However, the stability of the solid may be compromised with time, and future use of the disposal site is limited (USEPA 2000). Bioremediation, by disposing of the waste onsite or offsite on land, enables the oil in the drill cuttings to be biologically degraded using naturally occurring or introduced hydrocarbon-degrading microorganisms in the soil (AEUB 1996; USEPA 2000). One major drawback is the extensive time required for satisfactory remediation (USEPA 2000). Drill cuttings could also be re-injected into underground oil-bearing formations, away from the groundwater (USEPA 2000; CAPP 2001). However, if re-injection is not technically or economically feasible, the wastes must be treated to reduce oil concentrations prior to final disposal. Cleaning involves separating the pollutant from its mineral substratum by solvent washing or thermal means. Solvents include surfactants, ammonia, freon and propane, which generally generate other waste streams that need to be treated. Solvents also have safety, efficiency and environmental concerns (Eldridge 1996). Incinerating the waste has high-energy use problems (Tomasko *et al.* 1995; USEPA 2000).

The solvent extraction process using environmentally-friendly, inert, cheap, widely-available, inflammable and non-explosive carbon dioxide at or above its supercritical conditions of 31.3°C and 7.38 MPa to treat oil-contaminated drill cuttings is very promising (Lee and Gongaware 1997; 1998; Saintpere and Morillon-Jeanmaire 2000b). Supercritical carbon dioxide (SC CO_2) exhibits excellent solvating characteristics

which are easily manipulated (Bright *et al.* 1992) to dissolve non-polar compounds, such as diesel and mineral oils.

SC CO_2 technology has been extensively used (Chester *et al.* 1998) on a commercial scale for coffee bean decaffeination (Udayasankar *et al.* 1986; Peker *et al.* 1992; Ramalakshmi and Raghavan 1999), oil extraction from food and agricultural products (Illes *et al.* 1997; Valcarcel and Tena 1997; Eller and King 2000; Caredda *et al.* 2002), spice and natural flavour extraction (Miller *et al.* 1995; Peusch *et al.* 1997), specialty cleaning (Purtell *et al.* 1993a; 1993b) and the fragrance industry (Hawthorne *et al.* 1988; Walker *et al.* 1994) .

1.1 OBJECTIVES

The objectives of the research are to treat OBM drill cuttings with supercritical carbon dioxide (SC CO_2) on a lab-scale, establish optimal extraction conditions, and evaluate the extraction efficiencies of diesel/mineral oil from raw cuttings. Raw oil-contaminated drill cuttings will be used, rather than diesel-spiked matrices, as in the work of Lee and Gongaware (1997). Extraction efficiency criteria used is cuttings' petroleum hydrocarbon content before and after SC CO_2 extraction, rather than residual oil content (ROC, as in the work of Saintpere and Morillon-Jeanmaire 2000b). The cuttings' petroleum hydrocarbon content is used because Alberta Energy and Utilities board (AEUB) drilling waste disposal guidelines are based on the more stringent petroleum hydrocarbon analysis as outlined in CCME (2002), AEUB (1996), USEPA (1996a, b, c, d) rather than oil content analysis used in Saintpere and Morillon-Jeanmaire (2000a).

Effective and optimal application of SC CO_2 for the remediation of oil-contaminated drilling wastes would substantially make the use of OBMs more appealing to the drilling industry saddled with trying to balance the OBMs superior performance with its treatment and disposal requirements. Successful implementation of this remediation technology would afford the added benefit of recovering and reusing the expensive OBMs, eliminating the need for extensive land treatment. Successful application of this technology in offshore drilling locations would also help treat OBM cuttings offshore, eliminating the need for expensive transportation of the cuttings to shore. Research such as that outlined in this work will thus provide the necessary data to develop SC CO_2 extraction as an efficient solution to the problem of oil-contaminated drilling waste treatment and disposal. Supercritical CO_2 will then probably become the "green" solvent of the 21st century, and its large-scale use will provide an efficient solution to the problem of OBM cuttings treatment and disposal.

Chapter two of this work provides a review of literature relevant to the use and types of drilling fluids, solids control in drilling fluids, and treatment and disposal of drilling waste. In particular, supercritical fluid extraction is discussed in Section 2.5, as well as its applications in soil remediation. Chapter 3 is a discussion of the materials and methods used in this work for the laboratory treatment of centrifuge-underflow OBM cuttings using SC CO_2. The results obtained from this work and subsequent disussions are presented in Chapter 4. Also, conclusions from this work and suggestions for further work are discussed in Chapter 5.

CHAPTER 2 LITERATURE REVIEW

Canada is the third-largest producer of natural gas and the fourteenth largest producer of crude oil in the world with activities in the far north, east coast, oil sands and western Canada sedimentary basin (CAPP 2002). Oil and natural gas deposits are located almost exclusively in sedimentary rock (USEPA 2000). The province of Alberta, located in the Western Canada sedimentary basin, therefore accounts for a major fraction of the oil and gas deposits in Canada. In 2000, Alberta accounted for approximately 75% of Canada's $18 billion petroleum production, drilling and investment spending (CAPP 2002).

Exploratory activities are carried out to locate possible areas of significant oil and gas reserves. After a site has been judged to have a reasonable chance of discovering a sufficient amount of hydrocarbons, exploratory wells are drilled (USEPA 2000). These wells are followed by development, production, service and experimental wells, as required (USEPA 2000; CAPP 2002). In 2000, about 13,000 development, exploratory, oil sand and experimental wells were drilled in Alberta (CAPP 2002) with an average depth of 1.1 km per well. In the US, the range of depths of well holes is anywhere between 0.3 and 9 km, with an average depth of all U.S. wells drilled in 1997 of 1.7km (API 1998).

Oil and gas drilling rigs achieve drilling through the use of drill bits, strings and fluids (ADITC 1997; USEPA 2000). The drill bit is the component in direct contact with the rock at the bottom of the hole, and increases the depth of the hole by chipping off pieces of rock (US EPA, 2000). The drill bit is connected to the surface by several

segments of hollow pipe, which together are called the drill string (USEPA 2000). The drill string is usually about 10 cm in diameter. Drilling fluid, typically drilling mud, is pumped down through the center of the drill string and returns to the surface through the space, called the annulus, between the drill string and the rock formation or casing (USEPA 2000).

The following sections describe the importance and types of drilling fluids usually used in the drill operation. Typical drilling fluid additives and their functions are also discussed. Section 2.3 is a discussion of the importance of solids control in the drilling operation, and the typical equipment used to achieve the required solids control in the drilling mud. Section 2.4 discusses the various drilling waste treatment and disposal options currently available in Alberta, as well as current and cutting-edge worldwide practices. Section 2.5 discusses the supercritical fluid extraction as applicable to extraction of organics and oils from contaminated soils and cuttings.

2.1 DRILLING FLUIDS

Drilling fluid is an important component of the drilling process (USEPA 2000; CAPP 2001), and is required to:

i. cool and lubricate the drill bit;

ii. remove the rock fragments, or drill cuttings, from the drilling area and transport them to the surface;

iii. counterbalance formation pressure to prevent formation fluids (i.e. oil, gas, and water) from entering the well prematurely, and

iv. prevent the open (uncased) wellbore from caving in (Berger and Anderson 1992)

Different properties may be required of the drilling fluid, depending upon the drilling conditions. For example, a higher-density fluid may be needed in high-pressure zones, and a more temperature-resistant fluid may be desired in high-temperature conditions (USEPA 2000).

Air and foam fluids may be used in drilling wells on land. These fluids are less viscous than drilling muds and can enter smaller pores more easily (USEPA 2000). Air and foam fluids are used when a higher rate of penetration into the formation is desired (USEPA 2000), and only in relatively low-pressure and water-free drilling locations (Kennedy 1983). This is because the viscosity of air can be altered if drilling encounters liquid in the formation, and because air is less dense than a liquid, it cannot exert the same pressure in the hole as liquid (USEPA 2000). Also, air and foam fluids are preferred in these situations because they are much less expensive than other fluids (Kennedy 1983). Air and foam fluids typically do not contain many additives because the additives are either liquid or solid, and will not mix with air or foam drilling fluids. Air and foam fluids currently are used in the drilling of approximately seven percent of the wells in the United States (API 1997).

The three general categories of drilling muds are water-based, oil-based, and synthetic-based (AEUB 1996; USEPA 2000).

2.1.1 Water-Based Muds (WBMs)

Of the three types of muds, water-based muds are used most frequently (USEPA 2000). The water base may be either fresh or salt water, for onshore and offshore wells, respectively, and are therefore also called aqueous fluids (AFs) (CAPP 2001). The primary benefit of water-based muds is cost: water-based muds are the least expensive of the major types of drilling muds (non-aqueous fluids can cost between $250-$2,500/m^3) and in general they are less expensive to use since the resultant drilling waste can be discharged onsite provided these wastes pass regulatory requirements (C-NOPB 1998; USEPA 2000). The significant drawback with water-based muds is their limited lubricity and reactivity with some shales (USEPA 2000; CAPP 2001). In deep holes or high-angle directional drilling, water-based muds are not able to supply sufficient lubricity to avoid sticking of the drill pipe. Reactivity with clay shale can cause the destabilization of the wellbore. In these cases of clay shale reactivity with water-based muds, oil-based and synthetic muds are needed (USEPA 2000).

2.1.2 Oil-Based Muds (OBMs)

Oil-based muds are composed primarily of diesel oil or mineral oil (USEPA 2000). Oil-based muds are well suited for the high temperature conditions found in deep wells because oil components have a higher boiling point than water (USEPA 2000). Also, oil-based muds are used when drilling through reactive (or high pressure) shales, high-angle directional drilling, and drilling in deep water. These situations encountered

while drilling can slow down the drilling rate, increase drilling costs or even make drilling impossible if water-based muds are used (USEPA 2000). Oil-based muds are more expensive than water-based muds (CAPP 2001). This higher cost, which includes the added burden of removing the oil from drill cuttings, available disposal options, and stringent regulatory requirements constitute a major demerit for the use of oil-based muds (USEPA 2000; CAPP 2001). In cases when oil-based muds are necessary, the upper section of a well generally is drilled with water-based muds and the conversion is made to oil-based mud when the situation requires it (CAPP 2001).

It is predicted that since the industry trend is toward deeper wells (USEPA 2000), oil-based muds may become more prominent (US EPA, 2000). One major hindrance to the increased use of OBMs would be the problem of disposal of OBM wastes, which cannot be disposed of as easily as WBMs. There is therefore the need for economical, efficient and environmentally acceptable treatment of these OBM wastes to make the use of OBMs more appealing to industry.

2.1.3 Synthetic-Based Muds (SBMs)

Since about 1990, the oil and gas extraction industry has developed many new oleaginous (oil-like) base materials from which to formulate high performance drilling muds (USEPA 2000). Examples of these synthetic base materials include vegetable oil esters, poly alpha olefins, internal olefins, linear alpha olefins, synthetic paraffins, ethers, linear alkylbenzenes, and others (USEPA 2000). SBMs, along with OBMs, are sometimes generally called non-aqueous fluids (NAFs) (CAPP 2001). Other oleaginous

materials have also been developed for this purpose, such as enhanced mineral oils and non-synthetic paraffins (USEPA 2000). Industry developed synthetic-based fluids with these synthetic and non-synthetic oleaginous materials as the base fluid, to provide the drilling performance characteristics of traditional drilling fluids based on diesel and mineral oil (USEPA 2000). With respect to OBMs, these synthetic-based muds have potential for lower environmental impact and greater worker safety through lower toxicity, elimination of polyaromatic hydrocarbons (PAHs), faster biodegradability, lower bioaccumulation potential and, in some drilling situations, decreased drilling waste volume (USEPA 2000; CAPP 2001).

Some of the limitations of SBMs include stability and cost. Individual thermal stability performances of SBMs depend upon the chemical structure of the base fluid (CAPP 2001). Traditional esters used as SBMs have been found to exhibit the lowest degree of thermal stability (CAPP 2001). Also, contemporary SBMs are constructed from manufactured chemical compounds that are usually three to five times more expensive than mineral oil (CAPP 2001). This higher cost is due to the fact that SBMs require more processing and have limited availability, while diesel fuel is widely used and remains relatively low in price (CAPP 2001).

2.2 DRILING MUD ADDITIVES

Drilling muds usually contain a weighting material to alter the density and increase the viscosity of the mud (Simpson 1986; USEPA 2000; CAPP 2001). Drilling mud may also contain additional additives that alter the properties of the fluid for the

particular requirement of the well being drilled. The following is a list of the typical additives and their uses (USEPA 2000):

i. Weighting materials, primarily barite (barium sulfate), may be used to increase the density of the mud in order to equilibrate the pressure between the wellbore and formation when drilling through particularly pressurized zones. Hematite (Fe_2O_3) is also sometimes used as a weighting agent in oil-based muds.

ii. Corrosion inhibitors such as iron oxide, aluminum bisulfate, zinc carbonate, and zinc chromate to protect pipes and other metallic components from acidic compounds encountered in the formation.

iii. Dispersants, including iron lignosulfonates, to break up solid clusters into small particles so the fluid can carry them.

iv. Flocculants, primarily acrylic polymers, to help suspended particles group together so they can be removed from the fluid once at the surface.

v. Surfactants, like fatty acids and soaps, to defoam and emulsify the mud.

vi. Biocides, typically organic amines, chlorophenols, or formaldehydes, to kill bacteria that may produce toxic hydrogen sulfide gas.

vii. Fluid loss reducers including starch and organic polymers, to limit the loss of drilling mud to under-pressurized or high-permeability formations.

A typical drilling mud formulation is therefore made up of a cocktail of several different additives required to ensure efficient drilling of the wellbore.

2.3 SOLIDS CONTROL

The drilling mud circulating and solids control equipment form a very essential part of the drilling operation (CAPP 2001). The level of cuttings (or drilled solids) in any drilling fluid must be controlled, as a high concentration will cause drilling problems

(CAPP 2001). As mentioned earlier, weighting materials (e.g. barite) are added to a mud system to achieve desired properties. Drill cuttings, on the other hand, are undesirable solids (CAPP 2001).

Efficient solids control optimizes the size, type and amount of solids in the drilling mud (CAPP 2001). A small fraction of the solids should be colloidal sized (<2 μm) for needed viscosity, as too high a concentration of these increases viscosity beyond the desired range (CAPP 2001). Also, solids in the drilling mud tend to be ground into finer and finer particles as the cuttings are being transported from the well bottom to the surface, and during solids separation, causing tremendous increase in wetted surface area (CAPP 2001). This increased surface area reduces the amount of free fluid, increases mud viscosity and reduces overall performance of the drilling mud (CAPP 2001). It is therefore very important to efficiently remove drill solids prior to re-circulating the drilling mud to reduce the grinding of the cuttings into finer particles.

If a solids control system is not working efficiently, the resulting buildup of very fine drilled solids in the active circulating system can also result in the disposal of large volumes of "used" fluid (CAPP 2001).

Normal solids control systems, using shale shakers, will typically discharge cuttings with less than 15% by weight of base fluid (CAPP 2001). Drilling rigs will often have more equipment for solids control, including a desander, desilter, or centrifuge. These allow the separation of finer drill solids from the drilling fluid.

Solids removal efficiency is higher with NAFs (OBMs and SBMs) than it is with WBMs, because larger and easier to remove cuttings are generated when drilling with

NAFs than with WBMs (CAPP 2001). A greater volume of discharge will be generated when drilling with WBMs than with NAFs because of (CAPP 2001):

i. larger volumes of cuttings generated from the hole enlargement, which result when drilling with WBM

ii. higher fluid volume required to drill a hole of same dimensions, and

iii. bulk discharge of whole WBMs.

2.3.1 Shale Shakers

These are the primary solids control devices, and are essentially vibrating screen separators. The mud and cuttings are routed to shale shakers once they reach the surface. Once on the shaker, the vibration transports the cuttings to the far edge of the screen, where they are discharged, while the mud flows through the screen and is collected for further processing and reuse.

Shale shakers are however unable to remove silt and colloidal-sized particles due to the typically large screen size used on them. Hence, other equipment is required to control fine and ultra-fine drill solids.

2.3.2 Centrifuge Separator

Centrifuges, which can produce very high G-forces (600-800 G) are used to separate very fine drill solids from the drilling mud (CAPP 2001). Centrifuges may also recover barite from the drilling mud. As a result, centrifuges are not flawless in

separating unwanted drill solids from mud containing barite. Nevertheless, the advantages in ensuring proper solids control outweighs its limitations (CAPP 2001).

2.4 DRILLING WASTE TREATMENT AND DISPOSAL

Further treatment of the drill cuttings is usually required to dispose these wastes in an environmentally acceptable manner. The Alberta Energy and Utilities Board (AEUB 1996) specifies that the rock cuttings must be analyzed to determine oil content, bulk density, pH, electrical conductivity (EC), major ions (Ca, K, Mg, Na, Cl), metals (B, Cd, Cr, Cu, Ni, Pb, V, and Zn) and sodium adsorption ratio (SAR) (Drinnan *et al.* 1987; AEUB 2002). This characterization is also used to ensure suitability for the chosen treatment and disposal method. The liquid sample, which is basically the drilling mud with additives, is usually recycled into the drilling process and re-used (USEPA 2000). At the end of the drilling process however, the drilling mud must be analyzed to determine the appropriate treatment and disposal methods (Drinnan *et al.* 1987; AEUB 1996). The Alberta Energy and Utilities Board also specifies that the pH, specific conductance, total suspended solids, nitrogen (nitrate and ammonia), major ions (Ca, K, Mg, Na, Cl), and SAR be determined for this purpose (AEUB 1996).

There are several methods currently available to deal with drilling waste treatment and disposal. In Alberta, the Drilling Waste Management Guide-50 (AEUB 1996) specifies different options based on whether the waste is derived from OBMs or WBMs. The first set of options are for mud systems other than oil based. These treatment options could be Onsite (Mix-Bury-Cover or Landspreading) or Offsite (Landspraying, Pump-

off, or Landspraying-While-Drilling) (AEUB 1996). The Land Treatment option is intended for oil-based (hydrocarbon) or saltwater-based mud systems. The onsite, offsite and land treatment options aim to incorporate the waste into the soil in a manner that (i) preserves the soil's chemical, physical and biological properties by limiting the accumulation of salts and hydrocarbons, (ii) does not harm the vegetation, and (iii) protects surface and groundwater quality (AEUB 1996). Guide 50 also allows for alternative disposal methods using new disposal technologies or new mud formulations, aside from the ones mentioned earlier, provided these new mud formulations are proven to have beneficial treatment and disposal advantages (AEUB 1996).

In addition to those identified by the Alberta Energy and Utilities Board above (AEUB 1996), other disposal methods used to deal with drilling waste include reinjection, reserve pit, incineration, solidification, commercial disposal, reuse/recycling, solvent washing and supercritical fluid extraction. It must be emphasized however that the permitted treatment and disposal methods for any type of drilling waste, at any place, depend on the disposal regulations established there (USEPA 2000; CAPP 2001).

2.4.1 Land Treatment

Land treatment is an environmentally acceptable (Barker *et al.* 1992; AEUB 1996; AEUB *et al.* 1996; AEUB 2002) drilling waste treatment and disposal method whereby wastes from one drilling site are applied onto a dedicated parcel of land (AEUB 1996). This parcel of land can only be used once (AEUB 1996). The land is managed in a manner that allows the soil system to biodegrade, transform and assimilate the many

organic compounds present in drilling waste (AEUB 1996; Chaineau *et al.* 1996; CAPP 2001), converting them to carbon dioxide and water (Riser-Roberts 1998; CAPP 2001) or less toxic end products. The land treatment disposal method, or an alternative disposal method, must be used when hydrocarbon-based mud systems have been employed (AEUB 1996).

Land treatment is an active practice that requires frequent tillage and application of nutrients to allow the indigenous soil microorganisms to optimally break down the hydrocarbons in the waste (Zimmerman and Robert 1991; AEUB 1996; CAPP 2001). Commercial microorganisms may be used if this allows the overall hydrocarbon degradation rate to be increased (Venosa *et al.* 1992; Korda *et al.* 1997). Organic amendments (e.g. manure, straw) are added to increase biological activity and aeration of the soil (AEUB 1996; Riser-Roberts 1998). Fertilizer may also be added as a microbial nutrient source to enhance microbial degradation of hydrocarbons (Riser-Roberts 1998). The primary process involved is biodegradation. However, significant volatilization may also occur (CAPP 2001).

Land treatment operations must be controlled to ensure that the hydrocarbons, salts and metals do not present a threat to groundwater or surface water, and that the hydrocarbon concentration does not inhibit biological activity (USEPA 2000). Such control involves regulating the hydrocarbon-loading rate on the area of land, and ensuring the land slope is not too steep to cause migration of contaminant. Proximity to surface or groundwater must also be checked to ensure surface or groundwater contamination is eliminated. Sampling and analysis are necessary to monitor the progress of the

remediation (AEUB 1996; Korda *et al.* 1997; Riser-Roberts 1998). Land treatment may be conducted onsite or offsite, in either the topsoil or the subsoil (AEUB 1996).

Landfarming enjoys a fairly significant amount of use in Alberta for drilling waste treatment and disposal (AEUB 1996; CAPP 2001) because of availability of large areas of appropriate land. It may however not be applicable in the more heavily populated areas, and rocky surfaces (CAPP 2001). Its use is also limited to the period of the year when the ground is not frozen, in regions with winter conditions (CAPP 2001; Margesin and Schinner 2001) and is impractical in cold climates with permafrost (CAPP 2001). In the US, approximately 10 percent of drilling waste solids is disposed of in landfarming operations (API 1997).

The Alberta Energy and Utilities Board (AEUB 1996) requires that the hydrocarbon content be reduced below 0.1 or 0.5% by weight (if the receiving soil is subsoil or topsoil) for land treatment site closure. An extensive amounts of time, land, continuous monitoring, operation and maintenance of the site to achieve this site closure criteria (USEPA 1987; AEUB 1996; Riser-Roberts 1998; USEPA 2000). Land treatment also poses the risk of long-term liability and potential surface and ground water contamination (CAPP 2001).

2.4.2 Composting

Composting is also a biodegradation technology (as is land treatment) in which the drilling wastes are mixed with a bulking agent (wood chips, manure, leaves, rice

hulls, etc.) to enhance aeration and microbial numbers, placed in a pile, and aerated (CAPP 2001). The mixture may be tilled (CAPP 2001) periodically to increase aeration, and nutrients or moisture may be added as needed (CAPP 2001). With composting however, high temperatures are generated in the pile, which further increase biodegradation rates and metabolic activity of the microbes, as well as volatilization of hydrocarbons (CAPP 2001). Composting serves as a viable alternative to land treatment in cases where space is limited and climatic conditions preclude year-round use of land treatment.

Potential sources of pollution from composting include air emissions from aeration, tillage and volatilization of hydrocarbons from wastes, and leaching of contaminants to surface and groundwater (CAPP 2001). Leachate must also be tested and treated if necessary. Wastes of high oil, salt or metals contamination may also inhibit microbial activity, and make the process less effective (CAPP 2001).

2.4.3 Bioreactors

If the potential hazards from discharges and VOC emissions are very serious, the likely bioremediation technology to use would be one involving an in-vessel system (Savage *et al.* 1985). An enclosed system would permit control of temperature, moisture, pH, oxygen, nutrients, addition of reactions and conditions, resulting in a more rapid and greater extent of biological degradation. This method is less dependent on favorable weather conditions, and seasonal fluctuations would not be a limiting factor (Savage *et al.* 1985). Examples of bioreactors include bioslurry reactors, gravel slurry reactors,

tubular reactors, blade-mixing reactors, prepared-bed reactors, fermenters, and fungal compost bioreactor.

2.4.4 Biopiles

Soil can be excavated and placed in a treatment area, in mounds resembling large compost heaps. A covering over the piles prevents release of vapors to the atmosphere during the process (Mohn *et al.* 2001). Here, the soil can be periodically turned over for aeration, or a sprinkling system can add water, nutrients, and a source of oxygen. An optional vacuum aeration system would allow volatile compounds to be collected and treated, if necessary and the ability to control moisture can prevent soluble constituents from leaching (Riser-Roberts 1998). The treatment unit requires less area than landfarming, and optimal treatment conditions can be maintained to reduce the treatment time needed.

Mohr *et al.* (2001) investigated biopiles for onsite bioremediation of soil contaminated with diesel fuel at different sites on the Arctic tundra. The results were highly consistent, with extensive hydrocarbon removal occurred after one summer. Addition of ammonium chloride and sodium phosphate greatly stimulated hydrocarbon removal and indicates that biodegradation was the primary mechanism by which this was achieved (Mohn *et al.* 2001). The results show that on-site bioremediation of fuel-contaminated soil at Arctic tundra sites is feasible with biopiles.

2.4.5 Re-injection

Re-injection of drill solids into dedicated sub-surface waste disposal zones either by annular re-injection or by dedicated disposal wells may, in certain circumstances, be a viable option for the disposal of these wastes during oilfield development drilling activities (C-NOPB 1998; Bybee 2002). Re-injection deposits cuttings and mud into the earth (CAPP 2001). The cuttings must be ground to less than 100 µm, and conditioned as required (using viscosifiers), and injected at the required rate and pressure (CAPP 2001). The most critical step in the re-injection design process involves selecting a geological zone capable of accepting the wastes on a long-term basis (CAPP 2001) without the risk of leaks, and fresh water aquifer/groundwater contamination (Eldridge 1996).

2.4.6 Reserve Pit

During drilling on land, a pit is usually constructed onsite to hold drill cuttings and extra drilling fluid (USEPA 2000). Depending on geology and hydrogeology, reserve pits might be required to have geosynthetic or synthetic liners. Often the pit is intended only as a temporary holding vessel for drilling waste before being moved offsite for treatment and disposal; however, at some sites, the reserve pit is used as the final disposal site (USEPA 2000). When used as a disposal method after drilling is completed, the liquid is removed by suction or by evaporation (if in a dry climate) and the solid remnants are covered over with dirt. The liquids account for approximately 62 percent of

drilling waste by volume (USEPA 2000). Over two-thirds of the remaining drilling waste solids are disposed of by burying them onsite in the reserve pit (API 1997).

2.4.7 Landfilling

A landfill is an engineered waste burial site designed to prevent loss of content and is often lined to reduce the potential of leachate migrating to the subsurface (CAPP 2001). When closed, a landfill may be covered with an impervious cap and may be revegetated (CAPP 2001). This technology may not be acceptable in some areas since the contaminants are not treated and remain onsite (CAPP 2001). Also, the risk of eventual liability for landfill site, public perception, transportation and disposal cost to regions where landfills are acceptable, are all major demerits of this technology (CAPP 2001).

2.4.8 Solidification/Stabilization

Solidification is a modification of the reserve pit disposal method (USEPA 2000). When drilling is completed, the contents of the pit (i.e. drilling waste) is mixed with a cementing agent (Portland cement, fly ash, and/or kiln dust) and allowed to dry (USEPA 2000; CAPP 2001). The liquid in the pit does not necessarily need to be removed (CAPP 2001). Chemical interaction can range from simple absorption of liquids to complete encapsulation, changing the waste material to a stable powder (CAPP 2001). The

contents of the pit may also be solidified into a concrete-like block, which immobilizes the heavy metal components (USEPA 2000).

The solidification/stabilization process adds significantly to the bulk volume of the waste (USEPA 2000), but the primary limitations of this technology have been the negative effects of salts and hydrocarbons on the integrity of the stabilized waste matrix (CAPP 2001). High concentrations of organic compounds, salts, and bentonite interfere with the curing process (CAPP 2001). Also, the hydrocarbon and salts do not interact with the matrix, as they are physically rather than chemically bound (CAPP 2001).

In API's 1995 survey (API 1997), less than 1 percent of drilling waste volumes was disposed of in this manner. The stability of solid generated by this technique is compromised with time, and future use of the site is restricted (USEPA 2000).

2.4.9 Thermal Treatment Technologies

2.4.9.1 Thermal desorption

This treatment technology is used to treat OBMs and SBMs and their cuttings that contain a recoverable quantity of base mud (CAPP 2001). The process uses a dryer to heat and vaporize oil and water, which are subsequently cooled and condensed back to a liquid state (CAPP 2001). The liquids are afterwards separated by gravity. The ideal end product is solids with no residual oil and water, which are disposed of in a landfill (CAPP 2001).

Thermal desorption is energy intensive, and produces secondary waste streams (air pollutants) including uncondensed vapors and dusts (CAPP 2001). High cost is also a primary limitation (CAPP 2001).

2.4.9.2 Incineration

Incineration uses very high temperatures to destroy organics and remove all water from drilling waste (CAPP 2001). A rotary kiln is usually used, which tumbles the waste and provides extensive contact with hot burner gas (USEPA 2000; CAPP 2001). The gas from the kiln passes through an oxidizer, wet scrubber and bag house before being vented to the atmosphere (CAPP 2001).

Incomplete combustion of the hydrocarbons may occur, which may produce polyaromatic hydrocarbons (PAHs) or formaldehydes in the waste gas stream (CAPP 2001). Also, ash from the incineration of solids may contain high levels of metals, uncombusted hydrocarbons, or PAHs (CAPP 2001). Incineration is also prohibitively expensive, generates additional waste streams and has safety concerns (USEPA 2000; CAPP 2001).

2.4.10 Commercial Disposal

Offsite disposal of drilling wastes by commercial enterprises accounts for disposal of approximately 15 percent of drilling waste solids in the US (API 1997). This

commercial disposal takes two formats depending on the level of oil and gas activity in an area. In major oil and gas producing areas, dedicated facilities for managing exploration and production wastes exist (USEPA 2000). These facilities manage drilling waste and some associated waste streams using a range of processes from landfarming to slurry injection of solids to disposal in salt caverns (USEPA 2000). Drilling wastes from offshore that cannot be discharged (e.g., from oil-based muds) typically are barged to shore and disposed of in these commercial facilities (USEPA 2000; CAPP 2001). In areas of the country with less oil and gas activity, municipal or commercial landfills may accept drilling waste and certain other waste streams (USEPA 2000).

2.4.11 Reuse/Recycling

A growing share of drilling wastes are reused or recycled (USEPA 2000). It is currently estimated that around 10 percent of total drilling waste volume (solids and liquids) are reused or recycled (USEPA 2000). The liquids (mud) are reconditioned, with solids and other impurities removed, and then used in the drilling of other wells. Because of the high cost of the base material, reuse of oil-based and synthetic-based muds is more common. Drilling waste is also used for landfill cover, and in roadbed construction, dike stabilization, and plugging and abandonment of other wells (USEPA 2000).

2.4.12 Offshore Discharge

Transporting the cuttings to shore from a remote offshore platform is very costly, and onshore disposal regulations are becoming more restrictive (Eldridge 1996). However, spent and excess water-based drilling muds (that meet regulatory requirements) may be discharged from offshore installations without treatment (C-NOPB 1998). Typically, the cuttings from the solids control equipment are flushed with water into a centralized discharge pipe that extends beneath the water surface (CAPP 2001), and released into the water environment.

Existing information suggests that synthetic-based drilling muds are relatively non-toxic in marine environments and have a high potential to biodegrade (C-NOPB 1998). OBMs and SBMs remaining from a drilling mud changeover or drilling program completion should be recovered and recycled, re-injected into the producing formation, or transferred to shore in an approved manner (C-NOPB 1998). Drill solids from operations that use diesel or similar highly aromatic oils as the continuous phase of the drilling fluid should not be disposed of into the sea (C-NOPB 1998).

2.4.13 Other Offshore Technologies

These are other lesser-used, and in some cases unproven drill waste management and disposal technologies promoted by various vendors for use offshore and onshore (CAPP 2001).

2.4.13.1 Hammermill

In the hammermill process, the oil-contaminated cuttings and mud is treated by frictional grinding in a sealed chamber such that sufficient heat is generated at 270-290 °C to flash evaporate both oil and water, leaving the dry powder (CAPP 2001). No combustion occurs in this process (CAPP 2001). The remaining powder in the vapor stream is separated by a cyclone, and the vapor is condensed to separate the oil and water, for reuse and discharge, respectively (CAPP 2001). The discharged powder would be similar in grain size to barite, and would be dispersed offshore similarly to WBM (CAPP 2001).

This technology is presently being used onshore in the UK and is expected to be implemented offshore (CAPP 2001). This process is currently limited by its inability to process large volumes of cuttings (CAPP 2001).

2.4.13.2 Silicate encapsulation

This treatment method is also called Silica Micro Encapsulation (SME). It involves removing the oil attached to the contaminated drill cuttings by emulsification in an acidic environment (Quintero *et al.* 2001) and then physically encapsulating or "sealing off" the cuttings within an insoluble matrix of amorphous silica (CAPP 2001; Quintero *et al.* 2001). Laboratory and pilot tests (Quintero *et al.* 2001) of the SME technology show that, using environmentally acceptable emulsifiers, oil-based mud

present on drill cuttings is removed and forms a stable oil-in-water emulsion. The encapsulated cutting may then be disposed of offshore (CAPP 2001). Over a period of time however, the silicate shells may break down, resulting in gradual release of oil to the environment (CAPP 2001). It is however also anticipated that slow oil release and dispersion would allow time for biodegradation of the oil through natural mechanism without creating anaerobic conditions on the seafloor (CAPP 2001).

2.4.12.3 Solvation

Solvation involves using a solvent to "wash off" the oil from contaminated cuttings (CAPP 2001), and it could occur at normal or elevated temperatures and pressures. The contaminant is removed from the cuttings into the solvent during the solvation, leaving cleaner cuttings that can then be disposed offshore, if applicable disposal requirements are met. This technology can also be applied on land.

Starosud *et al.* (2001) used an in-situ generation of surfactants, which wash out the hydrocarbon from the oil-contaminated drill cuttings after a mechanical stirring technique is applied. The treatment step involves mixing the cuttings with water, and a pre-determined amount of base. After a few minutes of intensive stirring, three phases are generated, which are the floating hydrocarbon, the "clean" cuttings and water, which can then be separated and disposed of or re-used (Starosud *et al.* 2001) . The obvious disadvantage of this process is the potential introduction of additional contamination (surfactants) into the drill cuttings, and generation of other waste streams, which have to be disposed of in an acceptable manner.

2.5 SUPERCRITICAL FLUID EXTRACTION (SFE)

2.5.1 Definition of a Supercritical Fluid

In the Pressure-Temperature (PT) diagram shown in Figure 2.1, phase lines separate the solid, liquid and gaseous phases of a particular substance. Sublimation (from solid to gas), melting (from solid to liquid) and evaporation (from liquid to gas) are transformations widely known and encountered everyday. The point where the solid, liquid and gaseous phases coexist is called the triple point.

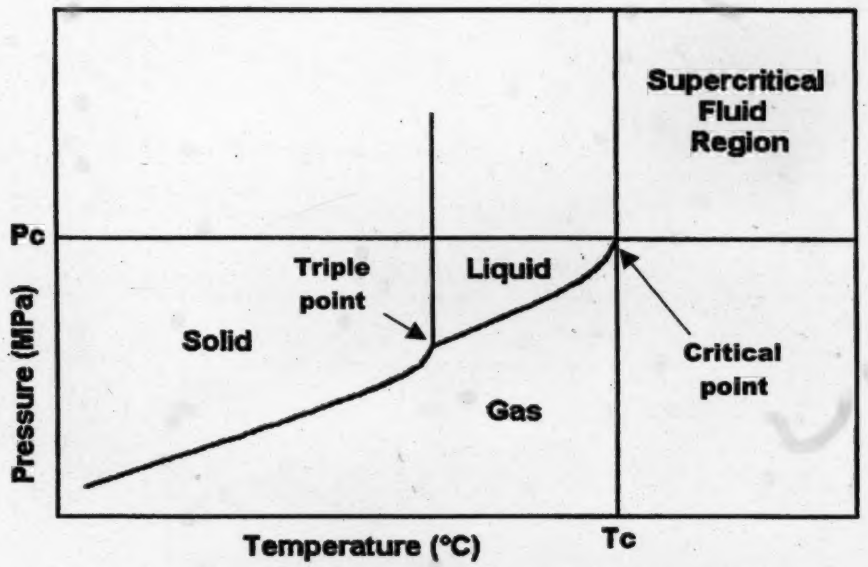


Figure 2.1: The Pressure-Temperature phase diagram for a fluid, illustrating the supercritical fluid region

As the temperature and pressure increases along the gas-liquid co-existence curve, the liquid becomes less dense because of thermal expansion and the gas becomes denser

due to pressure rise (Clifford 1999). The distinction between the gas and liquid phases eventually disappears as the densities of the two phases become identical. The curve therefore comes to an end at the ultimate point of the evaporation line called the critical point (Clifford 1999; Saintpere and Morillon-Jeanmaire 2000b).

When a substance is therefore heated and maintained above its critical temperature, it becomes impossible to liquefy it with pressure (Reid *et al.* 1987). When pressure is applied to this system above its critical pressure, a single phase is formed and exhibits unique physicochemical properties (Bruno and Ely 1991; McHugh and Krukonis 1994). This single phase is termed the supercritical phase and is characterized by a critical temperature and pressure (Tc and Pc), as indicated in the PT diagram (Figure 2.1). The region above the critical temperature (Tc) and pressure (Pc) is therefore called the supercritical fluid region, shown by the vertical and horizontal lines from the Pc and Tc.

Supercritical fluids offer a convenient means to achieve solvating properties, which have gas-like and liquid-like characteristics without actually changing chemical structure (Bright *et al.* 1992). The properties are intermediate between those of a liquid and gas (Table 2.1), with liquid-like densities and solvating powers, and gas-like diffusivities and viscosities (Vanwasen *et al.* 1980; Bright *et al.* 1992; Saintpere and Morillon-Jeanmaire 2000b). The solvating powers of supercritical fluids mimic a variety of liquid solvents but with zero surface tension.

By proper control of pressure and temperature, a considerable range of these physicochemical properties (density, diffusivity, viscosity, etc.) can be accessed without a phase change (Bright *et al.* 1992). A supercritical fluid can therefore be considered a continuously adjustable solvent with a single fluid phase (Bright *et al.* 1992).

Table 2.1: Thermophysical Properties of Supercritical Fluids vs. Gases and Liquids (Vanwasen *et al.* 1980; Bright *et al.* 1992)

Fluid State	Thermophysical properties		
	Density (g/cm^3)	Diffusion coefficient (cm^2/s)	Viscosity (g/cm.s)
Gas	10^{-3}	10^{-1}	10^{-4}
Supercritical fluid	0.1 - 1	$10^{-3} - 10^{-4}$	$10^{-3} - 10^{-4}$
Liquid	1	$< 10^{-5}$	10^{-2}

Freon, ethylene, ethane, propane, ammonia, methanol, ethanol, benzene, toluene, argon, xenon, freon, and carbon dioxide have all been used as supercritical fluids (Eldridge 1996; Chester *et al.* 1998; Saintpere and Morillon-Jeanmaire 2000b). All of these fluids, except for ammonia, exhibit critical pressures below 7.5 MPa, while critical temperatures for ethylene, ethane and carbon dioxide are below 35°C. However, most of the above-mentioned fluids, except carbon dioxide, are flammable, toxic, expensive, environmentally unfriendly or not readily available (Eldridge 1996; Saintpere and Morillon-Jeanmaire 2000b). With a critical temperature and pressure of 31.3°C and 7.38 MPa therefore, critical conditions of carbon dioxide are reached at a relatively lower temperature and pressure, as compared to the other fluids. Operational use of supercritical CO_2 (SC CO_2) is also favorable as carbon dioxide is non-toxic, inexpensive and inflammable. SC CO_2 does not leave any additional contamination on the treated matrix, and is therefore an environmentally friendly substitute for other organic solvents. CO_2 is

widely available and cheap, as it is obtained in large quantities as a by-product of fermentation, combustion, and ammonia synthesis (Clifford 1999).

The polar characteristics of CO_2 as a solvent are intermediate between a truly non-polar solvent (such as hexane) and weakly polar solvents (Clifford 1999). CO_2 is often classified as a non-polar solvent because the molecule is non-polar. It therefore dissolves a wide range of non-polar organics, including hydrocarbons and oils (Chester *et al.* 1998; Cocero *et al.* 2000). However, CO_2 has some limited affinity for polar solutes because of its large quadrupole moment (Clifford 1999). Indeed, pure CO_2 can be used as a solvent for many organic solute molecules (e.g. fluorinated compounds) even if they have some polar characteristics (Clifford 1999). SC CO_2 effectively removes polycyclic aromatic hydrocarbons (PAHs) (Barnabas *et al.* 1995; Hollender *et al.* 1997), chlorinated hydrocarbons and phenols (Ashrafkhorassani *et al.* 1995), pesticide and herbicide contaminants (Stuart *et al.* 1996) from soils (Chester *et al.* 1998). To further improve its affinity with polar molecules, CO_2 is sometimes modified with polar entrainers or modifiers such as methanol (Clifford 1999).

Other modifiers may be added to change the solvent character of SC CO_2 to suit the desired application e.g. methanol is added to increase polarity; aliphatic hydrocarbons to decrease polarity; toluene to impart aromaticity; and tributyl phosphate to enhance the solvation of metal complexes (Clifford 1999).

Supercritical CO_2 extraction also possess the following advantages:

i. It is rapid.

ii. The solvent is easier to remove, usually by simple pressure reduction.

iii. Extraction can be optimized by simple pressure and temperature change.

iv. CO_2 is available, to be used as a pure or modified solvent, with its convenient critical temperature, cheapness and non-toxicity.

v. CO_2 can be recycled and reused in the extraction process.

vi. The extraction process does not introduce additional contamination on the treated sample.

The challenges to using SC CO_2 extraction involve the requirement for

2.5.2 SFE for soil remediation

SFE can be used as a soil remediation technique for soils contaminated with organics. To do this, the contaminated matrix is placed in a closed extraction chamber and exposed to the supercritical fluid (SCF). Enough time is allowed for the contaminant to dissolve in the SCF, and the SCF containing the organic is allowed to flow out of the closed system. The effluent SCF containing the contaminant from the closed system is then depressurized below its critical pressure. The dissolved contaminant "falls out" of solution due to the loss of solvating power by the SCF. The contaminant is now separated from the soil, and can be collected in a collection device.

Only few studies report on supercritical fluid extraction of oil from OBM drill cuttings. The relevant work is discussed in the following sections.

2.5.2.1 SC CO_2 extraction of diesel oil from an inert matrix

Most oil-based muds use diesel oil and their base fluid. The work done by Lee and Gongaware (1997; 1998) examined extraction of spiked diesel oil from Celite® (diatomaceous earth) using SC CO_2. Using a 10 mL stainless steel extraction vessel, Lee and Gongaware (1997; 1998) tested a range of pressures and temperatures from 20.3 to 50.7 MPa and 50 to 70°C, respectively. Total petroleum hydrocarbon (TPH) analysis of spiked and SC CO_2-extracted Celite® by gas chromatography/flame ionization detection (GC/FID) and weight difference were used as criteria for recovery evaluation. The greatest diesel oil recovery (more than 95% recovery of diesel fuel) was found to be at 30.4 or 35.5 MPa and 50°C for 30-minute extractions.

2.5.2.2 Supercritical fluid extraction of oil from drill cuttings

Using propane and freon

Eldridge (1996) did pilot plant testing for the extraction of oil-based drilling mud contamination from cuttings using supercritical propane and freon (1,1,1,2-tetrafluoroethane). The studies used a sample from a North Sea OBM drilling operation extracted in a 1-L heated stainless steel autoclave. Extraction times varied from 30 minutes to 3 hours and the mass of cuttings was approximately 260 g (Eldridge 1996). Pyrolysis gas chromatography was used to determine the level of oil contamination of the

drill cuttings (Eldridge 1996), and indicated oil-contaminant removal greater than 98%. Propane exhibited satisfactory levels of oil removal, using very fine drill cuttings (Eldridge 1996)

The use of SC Freon and SC propane processes however have safety and environmental acceptability problems. Propane is very flammable, while freon, as a CFC (chlorofluorocarbon), deteriorates the ozone layer above the atmosphere, thereby reducing the capacity of the earth to be shielded from dangerous radiations from the sun.

Using carbon dioxide

Supercritical carbon dioxide (SC CO_2) extraction was applied to different oily drilling cuttings from various locations using a 500 g-capacity unit (Saintpere and Morillon-Jeanmaire 2000b). Larger scale extractions using a 6 kg static reactor and a 10 kg rotating autoclave were also investigated (Saintpere and Morillon-Jeanmaire 2000b). Pilot scale extractions were carried out with 200 g cuttings per batch, and extraction temperatures and pressures ranging from 35 to 45°C, and 6 to 12 MPa respectively. Initial oil content (IOC) on raw cuttings was measured by a retort method (distillation), while very low residual oil content (ROC) was evaluated by a Rock Eval apparatus, measured by an FID (Saintpere and Morillon-Jeanmaire 2000a).

The work of Saintpere and Morillon-Jeanmaire (2000b) showed that the technology is efficient for various OBM and associated types of cuttings, with the obtained optimal conditions at 35°C and 10 MPa (Saintpere and Morillon-Jeanmaire 2000b). The effect of temperature increase was limited, while pressure increase above the

critical point considerably increased the treatment efficiency up to the optimal pressure of 10 MPa. The oil contents were reduced from between 6 to 13% to as low as 0.2% ROC by weight of dry cuttings (Saintpere and Morillon-Jeanmaire 2000b). ROCs below 1% were also reached using the two larger scale units, thus showing that scaling the process up from hundreds of grams to several kilograms was also viable and practical (Saintpere and Morillon-Jeanmaire 2000b).

The oil recovered by the SC CO_2 extraction process showed no alteration in oil composition and can be entirely re-used without any additional treatment (Saintpere and Morillon-Jeanmaire 2000b). Agitating the extraction vessel did not appear to be necessary, although this phenomenon was not extensively studied (Saintpere and Morillon-Jeanmaire 2000b).

2.6 SUMMARY

While a considerable number of options exist for the treatment and disposal of water-based mud drill cuttings, the case is not so for hydrocarbon- and oil-based mud (OBMs) drill cuttings. Except for land treatment, the majority of the onsite and offsite disposal methods discussed in this chapter are not intended for drilling wastes resulting from the use of oil-based muds. Biodegradation of hydrocarbons contained in OBM cuttings using land treatment and composting requires extensive time and monitoring, and is not practical in unfavorable climatic conditions or restricted land use situations. Reinjection, landfilling, and solidification/stabilization have questionable long-term integrity and significant risk of contaminant migration from the disposed matrix. Thermal desorption

and incineration consume a lot of energy, are expensive and generate secondary waste streams.

Supercritical fluid extraction (SFE) offers a more benign way of treating OBM drill cuttings. The supercritical fluid used as a solvent has properties intermediate between those of a liquid and a gas. The supercritical state allows for easy manipulation of extraction conditions and contaminant solubility in the supercritical fluid (SCF), and eventual separation of the SCF from the contaminant is also easily achieved. Use of some fluids such as freon and propane for SFE however have environmental, safety and flammability concerns. The use of carbon dioxide as a supercritical fluid, however, is very promising, due to the favorable characteristics of SC CO_2, including the fact that it is environmentally-friendly, inflammable, inexpensive, widely available, and does not leave additional toxic residue on the cuttings after extraction.

CHAPTER 3 MATERIALS AND METHODS

The following chapter outlines the materials and methods used to evaluate the extraction of diesel oil from OBM centrifuge underflow drill cuttings using supercritical carbon dioxide.

3.1 MATERIALS

The following sections present the chemicals and other materials used for this research.

3.1.1 Oil-based Mud Drill Cuttings

Centrifuge underflow drill cuttings were used for the extractions. These cuttings were supplied by Unique Oilfield Technology Services (UNOTEC), Calgary from their drilling waste management operations in active drilling sites in Alberta, Canada. These underflow drill cuttings are generated from centrifuges used to separate very fine cuttings and barites from the oil-based muds (Figure 3.1). Only one batch of cuttings was used for this work. The cuttings used were generated using an oil-based mud system with zero water content.

The cuttings are thick, dark and sticky (Figure 3.2) with a strong characteristic diesel oil smell. These cuttings were kept in glass sample jars with minimal headspace. The jars were Teflon™-taped and stored below 4°C in a refrigerator to eliminate volatilization of lighter hydrocarbons from the cuttings.

Figure 3.1: Underflow OBM cuttings generated from the centrifuge separator

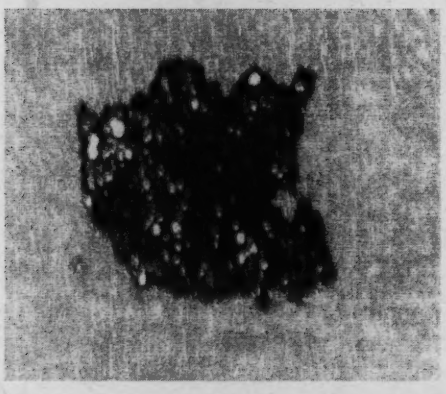


Figure 3.2: Centrifuge underflow cuttings used

3.1.2 Diesel Oil

Total petroleum hydrocarbon (C_{10}-C_{32}) content of the cuttings analyzed by gas chromatography/flame ionization detector (GC/FID) was used to measure SC CO_2 extraction performance. The diesel oil used to calibrate the GC/FID and prepare barite (inert matrix) spiked samples for analytical method quality control was also supplied by Unique Oilfield Technology Services (UNOTEC). The diesel oil was the same as that used for the base fluid for oil-based mud preparation at the drilling site (Laurel 2001), and has the characteristic smell of commercially available diesel oil. This diesel was kept in a glass sample jar with minimal headspace, Teflon™-taped and stored below 4°C (to eliminate volatilization of lighter hydrocarbons in the diesel oil) in a refrigerator prior to standards preparation.

3.1.3 Barites

For quality assurance of the GC/FID analyses, inert material spiked with diesel oil at a known concentration was analyzed. Naturally occurring barites ($BaSO_4$) was chosen as the inert matrix as it is also a major weighting additive of drilling muds.

A 40 kg bag of barites (SPARTON brand) by Mountain Minerals (a division of Highwood Resources Limited, Lethbridge, Alberta) was supplied by Unique Oilfield Technology Services (UNOTEC). This barite is the typical additive used as weighting material for oil-based muds (Laurel 2001).

3.1.4 Chemicals

Supercritical grade carbon dioxide (Praxair, Edmonton, Alberta) was used for the extractions. Methylene chloride (GC Resolv, Fisher Scientific, Nepean, Ontario) was used as a liquid solvent to clean the extraction vessel after extractions. Methylene chloride was also used in the second trap vials during extraction to collect any diesel oil not removed by the first glass wool trap vial (Figure 3.5 and descriptions in sections 3.2.1). Also, standards for alkane retention time determination, and diesel oil standards for GC calibration were all prepared in methylene chloride (GC grade, Fisher Scientific, Nepean, Ontario).

Octane (99+%, Acros Organics, New Jersey), decane (99+%, Acros Organics, New Jersey), hexadecane (99%, Acros Organics, New Jersey), and dotriacontane (99%, Acros Organics, New Jersey) were used for alkane retention time determinations, as described in Section 3.2.3.4.

3.1.5 Extraction vessel

The vessel used for the SFE extractions is a 300 mL 316 stainless steel bolted enclosure vessel supplied by Autoclave Engineers (Division of Snap-tite, Erie, Pennsylvania). The schematic of the vessel body and cover is shown in Figure 3.3 and Figure 3.4, respectively. The stainless steel vessel consists of the body, cover, seal ring (gasket) and socket head cap screws, with configuration as detailed by Autoclave Engineers (2001) and Savoie (2001).

There are three 1/8" NPT openings on the cover for inlet, outlet and thermistor probe, and are designated as A, B and C, respectively (Figure 3.3 and Figure 3.4). A 1/16" to 1/8" bored through stainless steel male connector (Swagelok Co., Solon, Ohio) was placed at the inlet (labelled A in Figure 3.3 and Figure 3.4). This bored through fitting allowed the 1/16" outside diameter, 0.05 mm inside diameter (ID) stainless steel tubing (Chromatography grade, Fisher Scientific, Nepean, Ontario) to extend to the bottom of the vessel.

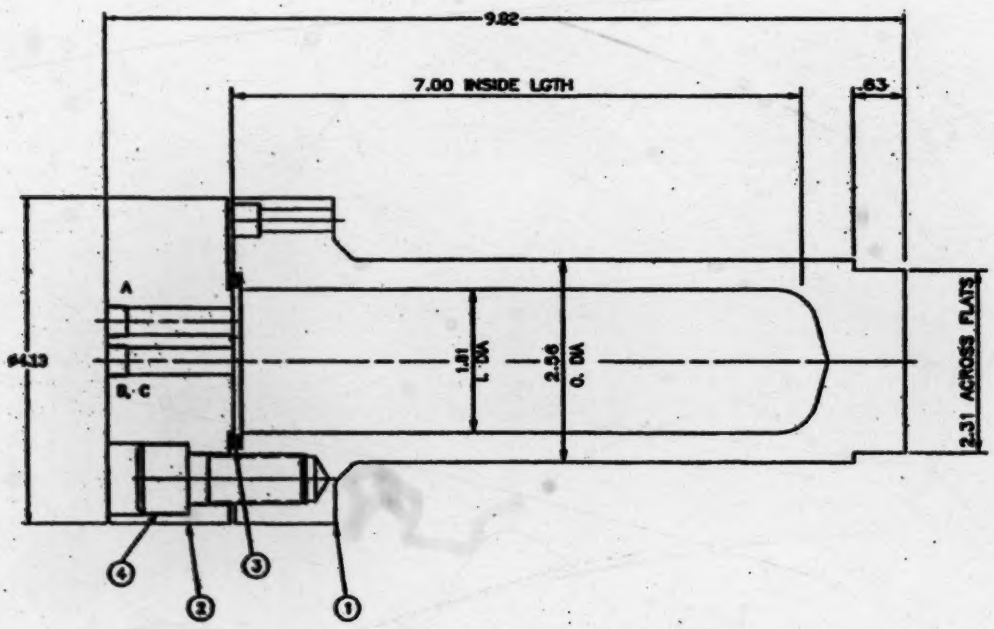


Figure 3.3: Pressure vessel (300 mL) used for SC CO_2 extractions (diagram supplied by Autoclave Engineers)

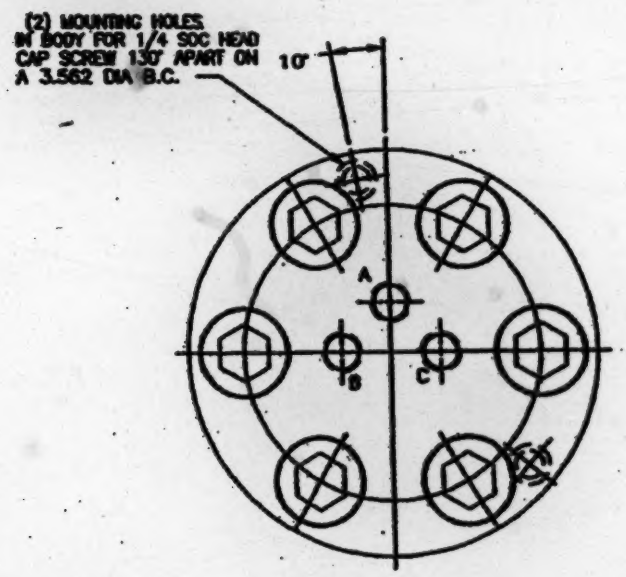


Figure 3.4: Pressure vessel cover (diagram supplied by Autoclave Engineers)

Although there was no distributor at the bottom, extending the tubing to the bottom of the vessel was to ensure that there was no "short circuiting" of the supercritical fluid entering the vessel i.e. that the supercritical fluid would flow throughout all of the vessel and not only the upper part. At the outlet, a l/16" to 1/8" NPT stainless steel male connector was placed to which a l/16" OD (0.05 mm ID) stainless steel tubing was attached. A 1/8" to 1/8" NPT bored through male connector was required at the third opening (labelled C in Figure 3.4) to place the 1/8" OD YSI 406 thermistor probe (Labcor Technical Sales, Inc., Concord, Ontario) inside the vessel.

To prevent leaks from occurring, Teflon™ tape was placed onto the threading of the male connectors before tightening them into the cover openings. Outlet B on the cover was also plugged with glass wool (Supelco, Bellefonte, Pennsylvania) to prevent entrainment of fine cuttings with the supercritical fluid during extractions. Limiting

particle entrainment ensured that process valves and tubing downstream of the vessel were protected from plugging with soil particles and fines.

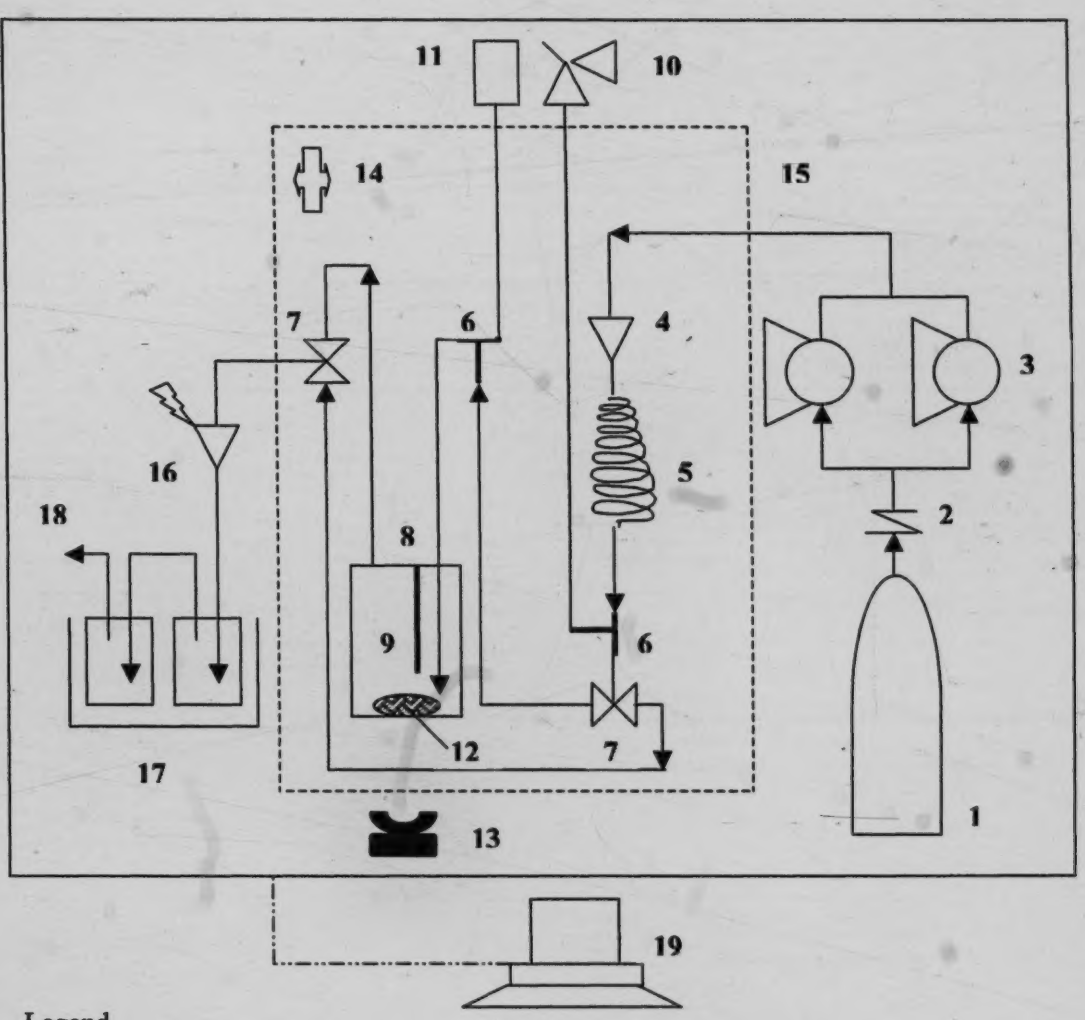
To assemble the vessel, the manufacturer's suggestions were followed whenever possible. From continuous use however, the seal ring (gasket) became permanently fixed on the vessel body, and could not be removed without damage to the vessel. This did not create any leakage problems because the vessel cover seals very well onto the body. The cover was then placed on top while ensuring that the opening for the screws on the cover and the vessel body were properly aligned. The bolts' threading were lubricated with Jet-Lube MP-50 Moly-Paste (Jet-Lube of Canada Ltd., Edmonton, Alberta) and threaded down firmly into the body using an Allen wrench. The screws were then tightened in the following sequence using a torque wrench (ATD Tools Inc., Edmonton, Alberta): tighten in an alternating pattern at a torque of 25 ft-lb_f; repeat at the same torque, change the pattern and tighten each bolt adjacent to the other. The torque is then adjusted to 35 ft-lb_f, and then 43 ft-lb_f and the whole tightening pattern repeated. This tightening pattern ensures even loading on the gasket and prevents leaks when running at high pressures.

3.1.6 SC CO_2 Extraction Apparatus

The schematic of the supercritical fluid extraction system is shown in Figure 3.5, and the main components, suppliers and applicable information are given in Table 3.1. Supercritical grade CO_2 (Praxair, Edmonton, Alberta) supplied at a cylinder pressure of around 5.86 MPa was used in the experiments. The CO_2 was passed through a filter and pressurized using an ISCO 500D continuous flow syringe pump. For efficient and good

operation, the pump heads were cooled to 7.5°C using a circulating refrigerated water bath and temperature control jackets. The main line enabled pressurized CO_2 flow from the pumps through 1/16" OD stainless steel tubing to a check valve, a heating coil, a mixing-tee connected to the pressure relief valve, a three-way ball valve, a mixing tee connected to the pressure transducer, and finally to the 300 mL extraction vessel described earlier. A 1/16" OD (0.05 mm ID) tubing led to the bottom of the extraction vessel, and the mixing-tees were of low dead volume. The check valve was used to stop any backflow of CO_2, and therefore protect the pumps. The first three-way ball valve allows flow to be directed to the vessel, or through the bypass line to a second three-way valve. The set-up until this point was identical to that used by Stroich (2001) and Savoie (2002).

The CO_2 leaving the extraction vessel also flows to a second three-way valve, which ended the separation of the main line and bypass line, and connects directly to the metering valve. The CO_2 is then depressurized through this heated metering valve. The 1/16" OD tubing was changed from 0.5 mm ID to 1 mm ID to minimize flow restriction downstream of the metering valve. The depressurized CO_2 then passed through two Teflon™-taped glass trap vials immersed in an ice-cold water bath. The first trap vial contained glass wool while the second contained methylene chloride. The first vial was used to trap the extracted oil, while the second one was to collect any more oil that wasn't removed by the first vial from the CO_2 flow. The CO_2 is thereafter vented into a fume hood.



Legend

1	Carbon dioxide cylinder	11	Pressure transducer
2	Filter	12	Magnetic stir bar
3	Continuous syringe pumps	13	Magnetic stirrer
4	Check valve	14	Heating circulator
5	Heating coil	15	Plexiglass bath
6	Tee	16	Heated metering valve
7	3-way ball valve	17	Trap vials in ice bath
8	Extraction vessel	18	CO_2 vent to fume hood
9	Thermistor probe	19	Data acquisition
10	Pressure relief valve		

Figure 3.5: Supercritical fluid extraction set-up

Table 3.1: SC CO_2 extraction system components

Component	Supplier	Pressure rating (MPa)
CO_2 cylinder	Praxair Canada, Inc. (Edmonton, Alberta)	
Filter (0.5 micron and 10 micron)	Edmonton Valve and Fitting (Edmonton, Alberta)	
Syringe pump (ISCO 500D)	Canberra Packard (Mississauga, Ontario)	25.9
Pressure relief valve (SS-4R3A)	Edmonton Valve and Fitting (Edmonton, Alberta)	41.4
Check valves (Nupro)	Edmonton Valve and Fitting (Edmonton, Alberta)	41.4
Ball valves (Whitey)	Edmonton Valve and Fitting (Edmonton, Alberta)	17.2
Pressure transducer (PX 502)	Omega (Laval, Quebec)	20.7
Vessel (300 mL, bolted closure)	Autoclave Engineers (Division of Snap-tite, Erie, Pennsylvania)	37.2
Thermistor probe (YSI 406)	Labcor Technical Sales, Inc. (Concord, Ontario)	
Heating circulator (HAAKE Dl)		
Metering valve (Nupro)	Edmonton Valve and Fitting (Edmonton, Alberta)	13.8
Connectors etc.	Edmonton Valve and Fitting (Edmonton, Alberta)	
Stainless steel tubing (1/16" OD, 0.05 mm and 1 mm ID)	Fisher Scientific (Nepean, Ontario), Supelco (Oakville, Ontario)	

The system was equipped with a pressure relief valve to ensure that the pressure never exceeded the set maximum value. A pressure transducer was used to monitor the system pressure. Most of the SC CO_2 extraction apparatus was placed in a heated circulating water bath that was used for temperature control.

The temperature inside the extraction vessel was monitored using a thermistor probe. Data for the vessel temperature (as measured by thermistor probe), pressure (from the pumps and pressure transducer) and flow of CO_2 (as measured by the pumps) was collected using LabView 5.1 (National Instruments, Austin, Texas) data acquisition program.

Some mixing was provided in the extraction vessel using a small 5/8'' magnetic stir bar, with the magnetic stirrer placed under the water bath, directly beneath the extraction vessel.

3.2 METHODOLOGY

The procedures used for the SC CO_2 extractions of oily drill cuttings and for the analysis of the raw and SC CO_2 extracted cuttings for petroleum hydrocarbon content is described in the following sections.

3.2.1 SC CO_2 Extractions

Supercritical CO_2 extraction experiments were conducted at the conditions presented in Table 3.2. Apart from the runs at 35 and 40°C for which only one SC CO_2 extraction run was conducted, two experiments were conducted at each extraction condition of cycle, temperature and pressure.

Table 3.2: Supercritical CO_2 extraction experimental conditions

Pressure (MPa)	Temperature (°C)			
	35	40	50	60
8.3	✓			
10.3	✓		✓	
12.4			✓	✓ *
13.8			✓	✓
17.2		✓	✓	✓

✓ Single cycle extraction condition
* Double cycle extraction condition

The extractions were performed according to the following protocol:

- place approximately 10 g of well-homogenized oil-contaminated drill cuttings and the magnetic stir bar at the bottom of the clean vessel;
- plug vessel cover outlet with glass wool, and bolt cover to vessel;
- place vessel in empty water bath and connect CO_2 inlet, outlet and thermistor probe;

- fill water bath and heat vessel to required temperature;
- flow CO_2 into vessel at desired pressure and start magnetic stirring;
- for single cycle extractions, allow a static extraction of 15 minutes, followed by a dynamic extraction of 30 minutes;
- for double cycle extractions, allow a static extraction of 15 minutes, followed by dynamic extraction of 30 minutes. Shut all valves again to allow another static extraction of 15 minutes, followed by another dynamic extraction of 30 minutes;
- after extraction, shut all valves, stop pumps, and depressurise vessel;
- collect treated cuttings from vessel into a sample vial for analysis;
- analyse "before" and "after" extraction cutting samples for petroleum hydrocarbon content (C_{11}-C_{32});
- calculate the extraction efficiency.

Before beginning the experimentation, drill cuttings samples were well mixed by hand using a spatula. Three sub-samples were then placed in vials for petroleum hydrocarbon analysis by GC/FID. For SC CO_2 extractions, a 10 g sample is placed in the vessel, along with a magnetic stir bar. This stir bar was used to achieve some mixing of the raw cuttings under supercritical conditions. The 10 g mass of cuttings used for extraction was chosen to ensure the stir bar could displace the thick pasty cuttings under supercritical conditions. The vessel outlet on the cover is plugged with glass wool to avoid the entrainment of fine particles. The water bath was filled to midway of the extraction vessel cover, allowing for good heating of the vessel and leak detection. All of the mixing tees, the 3-way ball valves, and the check valve were completely immersed in the water bath to ensure there were no leaks in the system.

The extraction involved a 45-minute cycle, consisting of one 15-minute static extraction followed by a 30-minute dynamic extraction. The static extraction is achieved by shutting all valves downstream of the vessel (i.e. no flow of SC CO_2 through the vessel with continuous stirring). The magnetic stir bar mixing was started when desired supercritical extraction conditions of pressure and temperature were reached in the vessel, indicating the start of the static extraction. The dynamic extraction is carried out by opening the 3-way valve and metering valve downstream of the vessel into the traps. The dynamic extraction is done at a SC CO_2 flow rate of 10 mL/min, as delivered by the syringe pumps.

LabView was used to monitor the vessel and pump pressure, vessel temperature, and pump flow rate. There was also a mercury thermometer placed in the water bath to monitor the water bath temperature so adjustments could be made (cooling with ice cubes, or turning the circulation heater off or on).

Once the extraction cycle was complete, flow of SC CO_2 to the vessel was stopped and the vessel was depressurized. The 30-minute dynamic extraction time at 10 mL/min was to ensure the entire 300 mL of SC CO_2 at equilibrium with the oily cuttings during static extraction flowed through the traps.

To ensure the metering valve was not plugged during the dynamic extraction, the heating rate of the variable autotransformer tape heater (Type 3PN1010, STACO Energy products Co., Dayton, Ohio) was increased to 60% of its maximum output voltage. This heating was done to ensure that the metering valve and the lines downstream of it were warm enough to prevent freezing and plugging of lines while CO_2 was being depressurized. Ensuring the lines were not plugged was very important to maintaining

stable flow rates from the pumps. Also, overheating of the metering valve and lines was avoided to ensure that there was minimal volatilization and/or loss of the oil components at the metering valve or traps.

The extracted oil was trapped in the first vial with glass wool, while the second vial containing methylene chloride ensured any remaining oil in the depressurized CO_2 was captured before the CO_2 is vented to the fume hood. The second trap is often refilled with methylene chloride during the run as this methylene chloride is stripped off during the dynamic extraction.

After the extraction, the cuttings were removed from the vessel and prepared for petroleum hydrocarbon analysis. This preparation required that the remaining petroleum hydrocarbons present in the cuttings be extracted into methylene chloride, to be thereafter quantified by GC. This will be discussed in further details in section 3.2.3.

3.2.2 LABVIEW

National Instruments LabView 5.1 software was used for data acquisition, as set-up by Savoie (2002), although it can also be used for data control, data analysis, and data presentation. This software uses a graphical programming development environment based on the G programming language (Savoie 2002).

Figure 3.6 shows the LabView screen of the program used in this work. Roy Gitzell, a technician in the Electronics Group of the Department of Civil and Environmental Engineering, University of Alberta, developed the program used in this

work. Data can be saved at different time intervals and can be averaged. It is possible to average only one type of data. For example, it is possible to average the pressure data, if required.

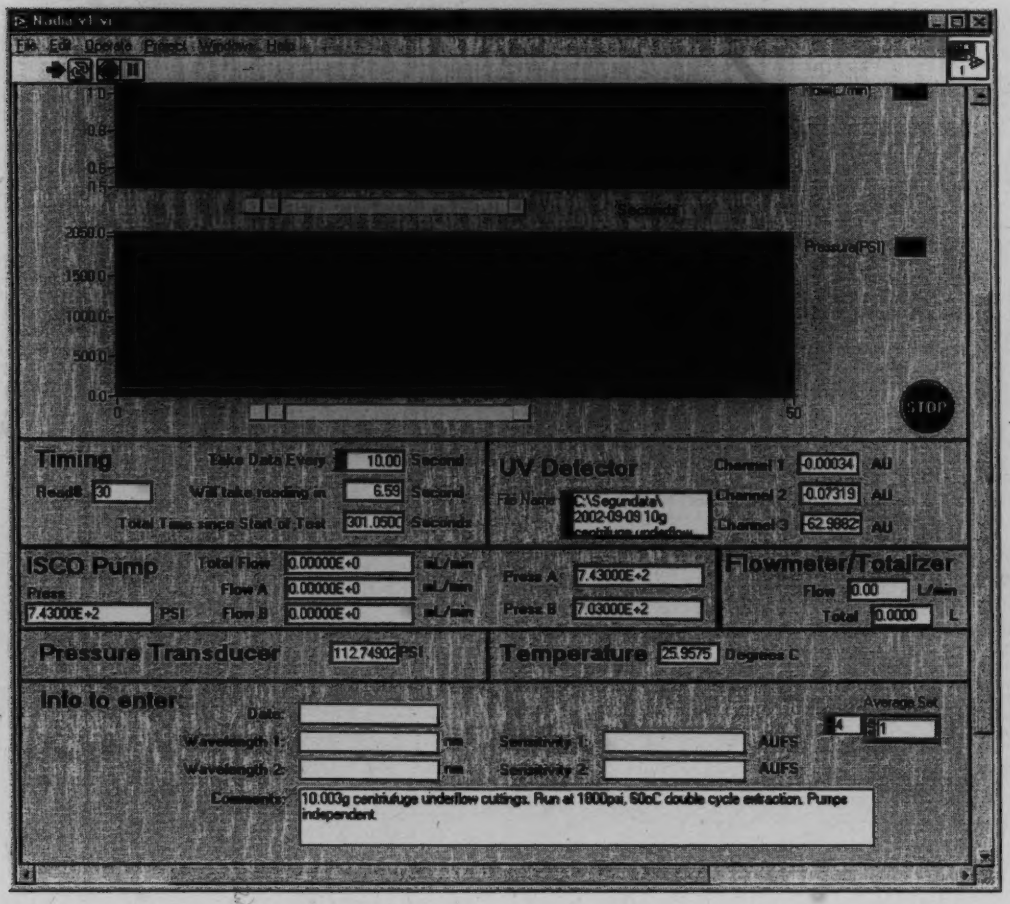


Figure 3.6: LabView Screen

Figure 3.6 provides an illustration of the average set box. Each number in the first box designates one of the types of data being saved that can be averaged and the second

box indicates the number of values to be averaged. The average value is then saved in the data file. The numbers on the left box in the average set box in Figure 3.6 is shown in Table 3.3, with the corresponding variables they represent.

Comments can also be added. These comments and the data are saved to an Excel file. The Excel file columns contain all the data collected by LabView. The relevant data and units are: scan number (or reading number, which is a serial number to identify the particular set of parameter values measured), time (s), pump pressure (MPa), pump flow (mL/min), transducer pressure (MPa), vessel temperature (°C), pump A flow rate (mL/min), pump B flow rate (mL/min), pump A pressure (MPa) and pump B pressure (MPa).

Table 3.3: Extraction variables and LabView averaging numbers (Savoie 2002)

Variable(s)	Number(s)
Pump pressure	0
Pump flow	1
Transducer pressure	2
Vessel temperature	3

3.2.3 Petroleum hydrocarbon (PH) analysis

The petroleum hydrocarbon content of the drill cuttings prior to and following the extraction was determined by gas chromatography (GC). The methodology used to

prepare the drill cuttings for GC analysis was modified from Lee and Gongaware (1997) and Zytner *et al.* (2001), which are adaptations of the United States Environmental Protection Agency SW-846 Method 3500B (for organic extraction and sample preparation), 3550B (for ultrasonic extraction), 8000B (for determinative chromatographic separations) and 8015B for non-halogenated organics using GC/FID USEPA (1996a, b, c, d).

Method 3500B provides general guidance on the selection of methods to be used in the quantitative extraction of samples for analysis by the semivolatile or nonvolatile determinative methods (USEPA 1996a).

Method 3550B is a procedure for extracting nonvolatile and semivolatile organic compounds (like diesel range hydrocarbons C_{10}-C_{32}) from solids such as soils, sludges, and wastes (USEPA 1996b). The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent. The method uses two different procedures, based on the expected concentration of organics in the sample. A larger sample size and a more rigorous extraction procedure is used for lower concentration samples (individual organic components of less than or equal to 20 mg/kg) because they are more difficult to extract. The medium/high concentration method (individual organic components of greater than 20 mg/kg) is much simpler and faster. This latter procedure was used in this work, as it is expected that the individual hydrocarbon contaminants in the drill cuttings would be greater than 20 mg/kg. Ultrasonic extraction is not as rigorous as Soxhlet extraction or other extraction methods for soils/solids (USEPA 1996b). Therefore, it was critical that the method (including the sonic-bath manufacturer's instructions) be followed explicitly in order to achieve the maximum extraction efficiency. This medium/high

concentration method involves mixing a 2 g sample with anhydrous sodium sulfate to form a free-flowing powder. This mixture is then solvent extracted once using methylene chloride and ultrasonic extraction. It is necessary to point out here that the horn-type ultrasonic disrupter device specified for use by this method (USEPA 1996b) was not used. Rather, a proven method used by Zytner *et al.* (2001) involving bath sonication and wrist-action shaking was used.

Method 8000B provides guidance on analytical chromatography and describes calibration and quality control requirements that are common to all EPA solid waste chromatographic methods (USEPA 1996c). This method, in conjunction with method 8015, was used for this work.

Method 8015B is used to determine the concentration of various nonhalogenated volatile organic compounds and semivolatile organic compounds by gas chromatography (USEPA 1996d). This method is also applicable to the analysis of petroleum hydrocarbons, including gasoline range organics (GROs) and diesel range organics (DROs) (USEPA 1996d). DROs correspond to the range of alkanes from C_{10} to C_{28} and covering a boiling point range of approximately 170°C – 430°C (USEPA 1996d). Commercial laboratory determinations for petroleum hydrocarbons however generally report C_{11} to C_{34} for diesel range petroleum hydrocarbons. The C_{10} to C_{32} alkane window was therefore chosen to be representative of the diesel range organics in this work. Method 8015 also suggests gas chromatographic conditions (USEPA 1996d), including appropriate column type and temperature program needed to separate the organic compounds. Fused silica capillary columns are necessary for the analysis of petroleum

hydrocarbons (USEPA 1996d). Detection is achieved by a flame ionization detector (FID).

In this work, preparation of the cuttings for petroleum hydrocarbon analysis involved the following steps (all carried out at ambient conditions):

- mix 2 g of raw or SC CO_2-extracted cuttings with 2 g of granular anhydrous sodium sulphate in a 20 mL Teflon™-taped amber glass vial;
- add 10 mL of methylene chloride to the vial;
- sonicate the vial for 30 minutes in a ultrasonic water bath;
- shake on a wrist-action shaker for one hour;
- pour the vial contents into a luer-tip syringe fitted with a filter holder and filtered into a 2 mL GC autosampler vial through a 1.0-micron filter paper in a holder.
- analyze the filtered extract by GC to determine the petroleum hydrocarbon content.

For each set of raw and SC CO_2-extracted drill cuttings, three sub-samples of 2 g each are extracted as outlined above. This extraction of sub-samples is performed to minimize variability in results due to the heterogeneous nature of the drill cuttings.

Some of the individual steps provided above are detailed in the following sections.

3.2.3.1 Bath sonication

After adding methylene chloride to the vial, the samples are sonicated for thirty minutes using a ultrasonic water bath (model FS20, Fisher Scientific, Pittsburgh,

Pennsylvania). This ultrasonic bath ensured intimate contact between the cuttings particles and the solvent due to the high-frequency ultrasonic vibration of the bath. The vials were clamped onto a retort stand, and suspended in the water bath of the ultrasonic cleaner. The sonication time was set to 30 minutes, based on the work by Zytner *et al.* (2001).

3.2.3.2 Wrist-action shaking

After sonication, the samples are clamped to a wrist action shaker (Model 75, Burrell Scientific, Pittsburgh, Pennsylvania) and shaken for one hour. The amplitude of shaking is set at 5, which is midway of the maximum on the shaker. This position was arbitrarily chosen to provide consistent amplitude of shaking from one batch of samples to another.

3.2.3.3 Filtration

Filtration of the solvent from the cuttings for GC analysis is achieved using a glass microfibre filter (Whatman International Ltd., Maidstone, England) fitted onto a stainless steel syringe filter holder (Model KS25, Advantec MFS, Inc., Dublin, California). The filter is binder free with characteristic particle retention of 1.0μm. This particle retention of 1.0μm gave sufficient particle separation, generating a visibly clear and particle-free filtrate adequate for GC injection. Also, the Canadian Association of

Petroleum Producers (2001) state that commercial barite used in drilling mud formulations have silt-like particle size varying from 2 to 74μm, while typical decanting centrifuges remove drilling mud particles as small as 1μm. It is therefore anticipated that the 1μm filter will remove all particles.

The extract is first poured into a luer-tip syringe fitted onto the filter holder, and then filtered into a 2 mL wide-mouth crimp-top GC autosampler vial. The vial is then capped and stored at 4°C in the refrigerator, ready for GC autosampler injection.

3.2.3.4 GC/FID method

At first, the GC analysis was performed using a manual-injection Varian 3300 Gas Chromatograph (Varian Inc., Mississauga, Ontario) equipped with a flame ionization detector (FID). However, results were difficult to analyze and interpret, because of the inevitable variability due to operator's manual injection of samples. Also, chromatogram plot and Area data presentation on paper by the integrator made data handling and analysis cumbersome. The integrator (Spectra-Physics model SP 4290, San Jose, California) also required specification of good integrator attenuation, which affects the chromatographic peak areas reported. The adequate attenuation to generate good chromatograms varied significantly from one sample to another. Also, peak area data had to be manually summed to establish the C_{10} -C_{32} chromatographic area. This manual summation allowed opportunity for calculation errors, especially in samples where a large number of peak areas were reported by the integrator. The GC/FID analyses using this equipment proved to be very strenuous and demanding, significantly limiting the

number of consistent and reliable GC/FID analyses done per day. Results generated by this equipment were not consistent with expected values reported by the industry (Laurel 2001) or with independent analyses by a commercial laboratory.

The use of a computer controlled Varian CP-3800 gas chromatograph (Varian Inc., Mississauga, Ontario) with CP-8410 model auto-injector equipped with an FID had a very positive impact on the accuracy, precision and turn-around-time of petroleum hydrocarbon analysis results. The Varian CP-3800 is a more recent GC, equipped with an autosampler. Work with this new GC necessitated understanding the equipment and related Star Chromatography Workstation Version 5 software, developing and testing appropriate programs, and completing sample injections and analysis.

Equipment calibration, sample injection, data analysis and calculations were done for raw and SC CO_2-extracted cuttings, method blanks, equipment blanks and spiked samples. Samples were also sent to Maxxam Analytics (Edmonton) for independent analysis to ensure quality control of in-house analyses.

Alkane and diesel standard preparation

Alkane standards were needed to establish the retention time for the C_{10} and C_{32} alkanes. Decane (C_{10}), hexadecane (C_{16}), and dotriacontane (C_{32}) were prepared individually at a concentration of 2000ppm (on a mass basis). The retention time between the C_{10} and C_{32} peaks constitutes the retention time window, which specifies the required diesel oil petroleum hydrocarbon range. These 2000-ppm standards were prepared by dissolving the appropriate amount of alkane in methylene chloride. Samples of these

standards were then placed in several 2 mL vials, capped and stored at 4°C in the refrigerator prior to GC injection.

Diesel calibration standards were also prepared at 150, 750, 1500, 9000, 15000 and 30000 ppm concentrations, which correspond to the expected working range of the GC. The standards were prepared by dissolving appropriate amount (weight) of diesel oil in methylene chloride. The methylene chloride was contained in a volumetric flask placed on an analytical balance (Model AX 205 delta range, Mettler Toledo, Columbus, Ohio). Samples were then placed in several 2 mL GC vials, capped and stored at 4°C in the refrigerator prior to GC injection.

GC/FID parameters

The Varian CP-8410 model auto-injector has a capacity for ten 2 mL autosampler vials and three 5 mL solvent vials. Pure GC Resolv methylene chloride was used in the solvent vials for injector syringe flushes. A total of six pre-injection and six post-injection solvent flushes were done per sample injection. Three sample flushes of the needle were also done prior to injection. The solvent sources were always replaced for each set of GC sample injections.

Of the ten sample vial positions available on the autosampler, eight were used for sample vials analysis per batch, with the ninth vial position for methylene chloride and the last one for diesel standard verification. Pure methylene chloride injections are done as blank injections required for sample area analysis, to clean the column between some samples, and to check false-positives due to sample carry-over in the GC column.

Standards are injected per batch, at a minimum of every 12 hours, to check for variations in chromatographic detections. GC/FID operation is checked and restored to normal if considerable variations are detected in standards analyses.

The CP-8400 GC parameters used in this work for diesel range petroleum hydrocarbon analyses include:

Carrier gas (Helium) flow rate:	7.0 mL/min
Makeup gas (Helium) flow rate:	30 mL/min
Injector temperature:	310°C
Injection volume:	1.0 µL
Injection mode:	Standard split/splitless
Split/Splitless Program:	
Initial:	Split state ON, with split ratio of 10
At 0.01min:	Split state OFF
At 1.00min:	Split state ON, with split ratio of 20
Column temperature program:	
Initial temperature:	50°C, hold for 2 minutes
Program:	50°C to 300°C, at 12°C/min
Final temperature:	300°C, hold for 12 minutes
FID Detector temperature:	340°C
Air flow rate:	300 mL/min
H_2 flow rate:	30 mL/min

The split/splitless injection mode is used, with an initial split ratio of 10. At injection, the split ratio turns off to prevent most of the methylene chloride solvent and diesel oil sample from being lost to the split bypass from the column. This possibility of loss of solvent and sample is considerable because of the high (310°C) injector temperature, which instantaneously vaporizes the volatile solvent and semi-volatile components of the diesel oil. The high injector temperature is however necessary to make sure heavier hydrocarbon components are vaporized and carried into the column. This injector temperature is similar to the 300°C used by Zytner *et al* (2001). Shutting the split

instantaneously after injection ensures almost all the sample is vaporized and carried onto the column. The split state is restored one minute after injection.

The CP-8400 GC also allows for electronic flow control i.e. all flow rates are set and controlled electronically without the need for manual valve regulation. Ultra-high-purity helium and hydrogen gases (Praxair, Edmonton, Alberta) were used, while the air (Praxair, Edmonton, Alberta) used is extra dry. These gas purities were used to ensure very minimal introduction of contaminants into the equipment.

Chromatogram peak measurements were made for detected species, and the FID noise is monitored before every injection. The initial signal to noise ratio is set at 100. This ratio allows only signals with peak values 100 times greater than the detected noise to be detected as a measurable peak.

GC calibration

The C_{10} and C_{32} alkane standards are injected according to the given GC/FID operating parameters to establish the retention time for these alkanes, thereby defining the C_{10}-C_{32} retention time window.

Diesel oil standards are also injected by the same method and data is stored for analysis by the Star Chromatography software. The diesel standard response used for calibration must represent the entire area of chromatogram within the retention time range established between C_{10} and C_{32}, including the unresolved complex mixture ("hump") that lies below the individual peaks (USEPA 1996d). This "hump" is due to the fact that although diesel fuel contains a large number of compounds that will produce

well-resolved peaks in a GC/FID chromatogram, the fuel also contains many other components that are not chromatographically resolved (USEPA 1996d). However, the area of the unresolved complex mixture also contributes an appreciable portion of the area of the total FID response (USEPA 1996d).

The area of all peaks eluting between the C_{10} and C_{32} is summed up. This summing is performed by projecting a horizontal baseline between the retention time of C_{10} and C_{32}. Also, because the chromatographic conditions employed for diesel range organics (DRO) analysis can result in considerable column bleed and a resulting rise in the baseline, it was appropriate to perform a subtraction of the column bleed from the area of the DRO chromatogram (USEPA 1996d). A methylene chloride blank is therefore analyzed during each analytical batch. The area of this chromatogram is measured in the same fashion as used for standards – by projecting a horizontal baseline across the DRO retention time range. This area is then subtracted from the area measured for the standards and the difference in area used to generate the calibration factor or curve (USEPA 1996d).

The detector response (area) is then plotted against the amount (concentration) of diesel range organics to generate the linear calibration using a least squares regression method (USEPA 1996d). During calibration, the Area (A) is treated as the dependent variable, and the standards concentration (C_{GC}, in ppm of diesel in methylene chloride) as the independent variable. The regression produced the slope and intercept terms for a linear equation, in the form:

$$A = a\,C_{GC} + b \qquad (1)$$

where: a = slope of the line (coefficient of C_{GC})
b = the intercept

The regression calculation generates a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. In order to be used for quantitative purposes, r must be greater than or equal to 0.99 (USEPA 1996d).

Sample and blanks injections

The 2 mL autosampler vials containing methylene chloride extracts of the raw and SC CO_2 extracted drill cuttings are injected in replicates (duplicates or triplicates) according to the exact chromatographic conditions used for standards calibration. The response area calculations are done in exactly the same way as for the diesel calibration standards, by summing the area between the C_{10} and C_{32} retention time window and subtracting the column bleed. The regression equation is rearranged to solve for the concentration (C_{GC}) of the injected sample extracts as:

$$C_{GC} = (A - b) / a \qquad (2)$$

Equation (2) was only used for samples whose integrated area was within the area measured for the calibration standards.

The concentration of petroleum hydrocarbon (C_{GC}) in the methylene chloride extract of samples is therefore established by the abovementioned protocol. The petroleum hydrocarbon content of the drill cuttings samples originally extracted must still be determined. Based on the extraction procedure outlined in section 3.2.3, it was

established that the drill cuttings hydrocarbon content ($C_{drillcutting}$, in percent petroleum hydrocarbon in cuttings), and GC-injected solvent extract hydrocarbon content (C_{GC}) are related by the following:

$$C_{drillcutting} = 0.0006825\ C_{GC} \quad (3)$$

Detailed calculations are presented in Appendix B3.

Quality control

Method blanks, which are samples that do not contain drill cuttings and sodium sulfate, but have followed the same methodology of solvent extraction, sonication, wrist-action shaking, and filtration, are also injected (in replicates) in the GC to investigate if positive errors are added by the method.

To confirm the accuracy of measured hydrocarbon contents, barites spiked with known amounts of diesel, are also solvent extracted and GC-injected in replicates. Sample blanks, which are pure barite samples presumably without any hydrocarbon content, are also solvent-extracted and analyzed to ascertain that barites have no substantial hydrocarbon content.

The calibration relationship established during the initial calibration must be verified at periodic intervals (USEPA 1996d). Calibration verification standards (diesel standards used for initial calibration) with known concentrations are therefore injected

per batch of ten autosampler vials to be injected. The percent drift is then calculated using these standards and the equation (4) below. The calibration is still considered valid if the calculated concentration is within fifteen percent of the response obtained during the initial calibration i.e. if the percent drift is less than 15%. However, if the calibration does not meet this limit, the instrument operating conditions are checked and if necessary, restored to the appropriate conditions. A new injection of the calibration verification standard is then done. The percent drift is defined as:

$$\%Drift = \frac{Calculated\ \ concentration - Theoretical\ \ concentration}{Theoretical\ \ concentration}\ X\ 100 \qquad (4)$$

Samples were also sent to Maxxam Analytic, an independent laboratory, for petroleum hydrocarbon (C_{11}-C_{34}) analysis. This commercial analysis was to confirm the efficacy and accuracy of the laboratory protocols and analysis developed in-house. The C_{11} – C_{34}, rather than C_{10} to C_{32} petroleum hydrocarbon content was performed at this independent laboratory, as this is the standard commercially available hydrocarbon analysis done for this range of petroleum hydrocarbons. The possible discrepancy in results due to the different hydrocarbon range is assumed to be minimal, as the major range of hydrocarbons (i.e. C_{10} to C_{28}) present in the samples is still being covered by the two analyses (in-house and independent laboratory).

CHAPTER 4 RESULTS AND DISCUSSION

The following chapter presents the results of the experiments conducted in this study.

4.1 SC CO_2 EXTRACTIONS OF CUTTINGS

Supercritical carbon dioxide extractions of diesel-range hydrocarbons from contaminated drill cuttings were conducted at temperatures between 35°C and 60°C, and pressures between 8.3 MPa and 17.3 MPa, to determine the optimal extraction conditions. To determine the efficacy of extractions at the threshold of supercritical conditions for carbon dioxide, whose critical conditions are 31°C and 7.4 MPa (Lemmon *et al.* 2001), the extraction conditions of 8.3 MPa and 35°C were investigated. Saintpere and Morillon-Jeanmaire (2000b) obtained optimal extraction conditions of oily drill cuttings at 35°C and 10 MPa, while Lee and Gongaware (1997) obtained optimal extraction conditions of spiked diesel oil at 50°C and 30.4 MPa or 35.5 MPa. Extraction conditions between 35°C and 60°C, and 8.3 MPa and 17.2 MPa were therefore investigated to establish the optimal conditions for this work, in comparison with previous work. Pressures above 24.1 MPa could however not be investigated because of the limitations of the syringe pumps used for this work. Pressures between 17.4 and 24.1 MPa were not investigated, because the results did not show appreciably higher increase in extraction efficiency with pressure increase from 12.4 MPa to 17.4 MPa.

The following sections describe the results obtained for the SCCO$_2$ extraction experiments. A sample Excel data file collected during an extraction experiment is given in Appendix A.

4.1.1 Pressure Data

ISCO syringe pumps and pressure transducer pressure data were collected with the LabView data acquisition software. The syringe pumps (A and B) pressure data indicate the pressure at which the pumps are delivering CO_2, while the pressure transducer data indicates the pressure immediately upstream of the extraction vessel. Figure 4.1 shows the sample pressure data for a single cycle extraction, while that for a double cycle extraction is shown in Figure 4.2.

Pumps A and B are run independent of each other, but simultaneously to ensure constant supply of CO_2. Pressure instability from the pumps prevents the pumps from being run in the Continuous Constant Pressure mode. The pressure transducer exhibits different offsets in comparison to the pressures of pumps A and B. The transducer readings usually indicate an offset of about +0.8 MPa when pump B is run first (or alone), and +0.4 MPa when pump A is run first (or alone).

In Figure 4.1, the pump pressures drop to that of the CO_2 cylinder, at around 6.1 MPa during the initial refilling of the pumps. The pressure transducer indicated a reading of 0.8 MPa existing in the flow line at the start of the extraction. With pump B started first, the pumps are then pressurized to the desired extraction pressure of 12.4 MPa at approximately 450 s. The pump pressure quickly rises to this desired pressure, and stabilizes in less than 60 s. The CO_2 flow is opened to the vessel at approximately 2200 s.

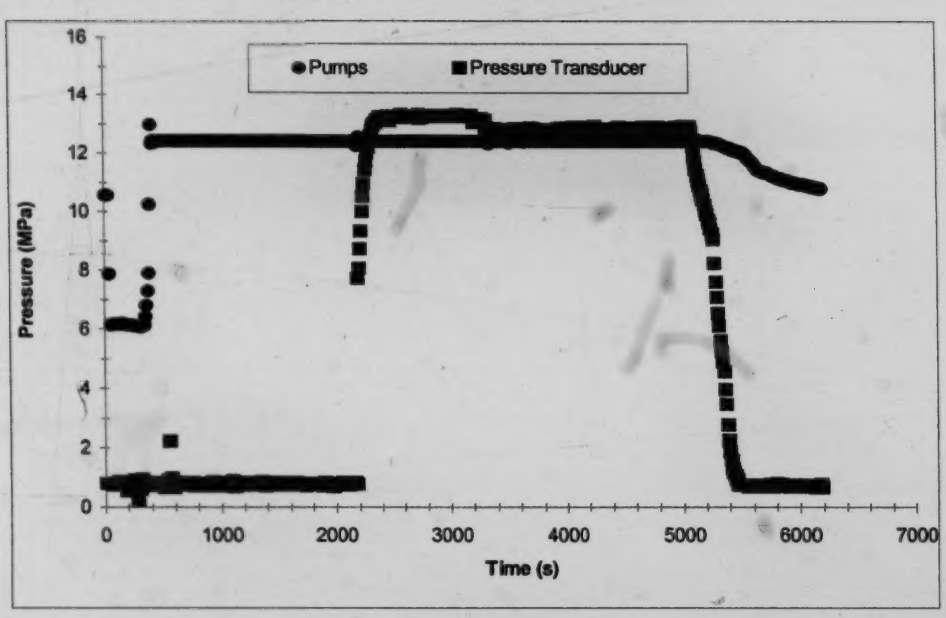


Figure 4.1: Sample pressure data for single-cycle SC CO_2 extraction (2002-06-18)

The vessel gradually pressurizes to about 13.3 MPa, as indicated by the pressure transducer, and stabilizes. This reading is 0.9 MPa more than the pump pressure of 12.4 MPa, but it is however in agreement with the repeatedly observed transducer reading offset of 0.8 MPa when pump B is run first, as mentioned above. The pressure transducer reading remains the same and steady until pump B runs out of CO_2 at approximately 3300 s and stops running. Because the two pumps were running independently of each other, pump A compensates for the loss of pump B and keeps the pressure steady at the required 12.4 MPa. The pressure transducer reading however indicates a drop from the previous 13.3 MPa reading to about 12.8 MPa. This 12.8 MPa measurement of the transducer is 0.4 MPa above the pump pressure of 12.4 MPa. This 0.4 MPa transducer offset is also repeatedly observed when pump A is running alone, as discussed earlier. The vessel pressure remains stable until the end of the extraction at about 5000 s when

the pumps are stopped and the vessel is depressurized. Once the vessel is completely depressurized, the transducer returns to the residual pressure of about 0.8 MPa originally found in the system.

The same observations made for the single cycle extraction were recorded for the double cycle, illustrated in Figure 4.2. At the end of the first cycle, the vessel is not depressurized as in the case of the single cycle extraction. Rather, all valves were kept shut and the pumps refilled from the CO_2 cylinder at around 5000 s. This refilling caused the pump pressure to drop to about 6.1 MPa, which is the pressure of the CO_2 cylinder. The pumps were then refilled and pressurized to 12.4 MPa.

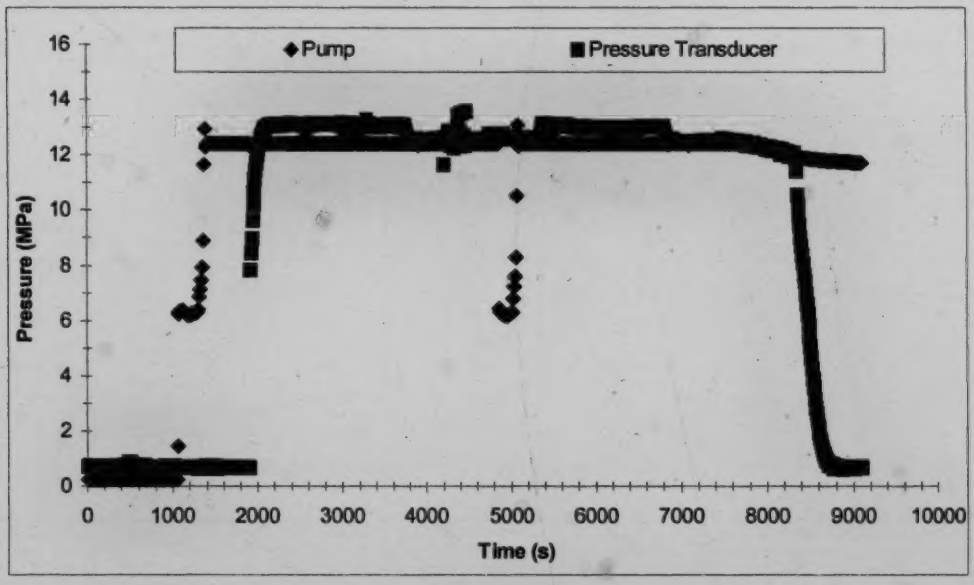


Figure 4.2: Sample pressure data for double-cycle SC CO_2 extraction (2002-08-19)

The pressure transducer again exhibited a positive offset of 0.8 MPa when pump B is running, and 0.4 MPa, when pump A is running, while the pump pressure remained stable throughout the extraction, except for when refilling and re-pressurizing the pumps. This

pressure transducer offset was observed during experimentation at all extraction conditions of temperature and pressure, suggesting that it is independent of the extraction conditions. The pumps are believed to be delivering the right pressure because they have been reset according to the manufacturers specifications at regular intervals.

4.1.2 Flow Data

Sample flow rate data for a single cycle extraction are shown on a large scale in Figure 4.3, and on a reduced scale in Figure 4.4.

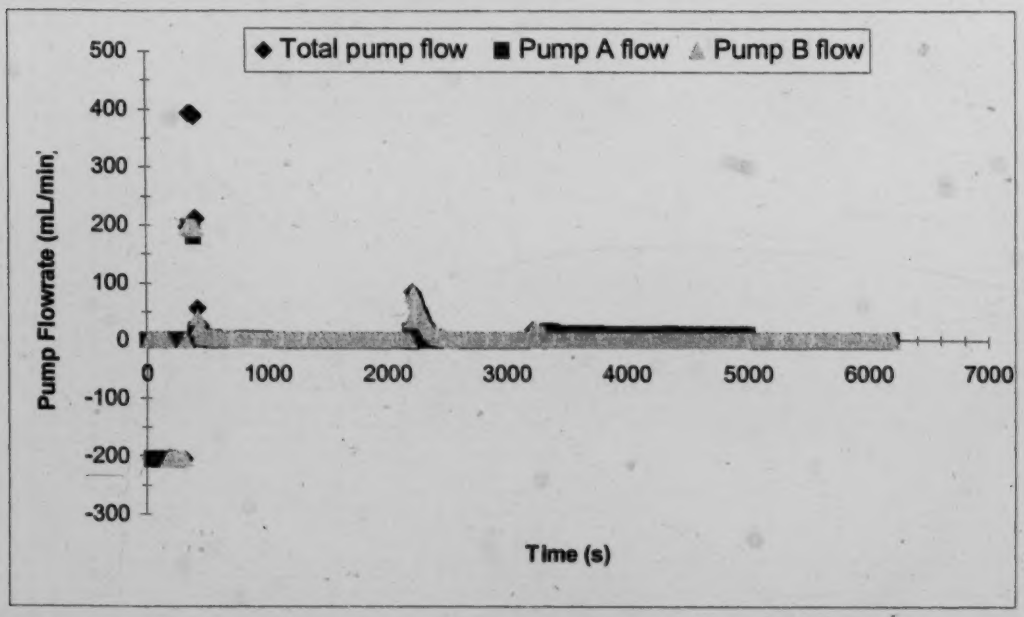


Figure 4.3: Pump flow data for single-cycle (2002-06-18) extraction (large scale)

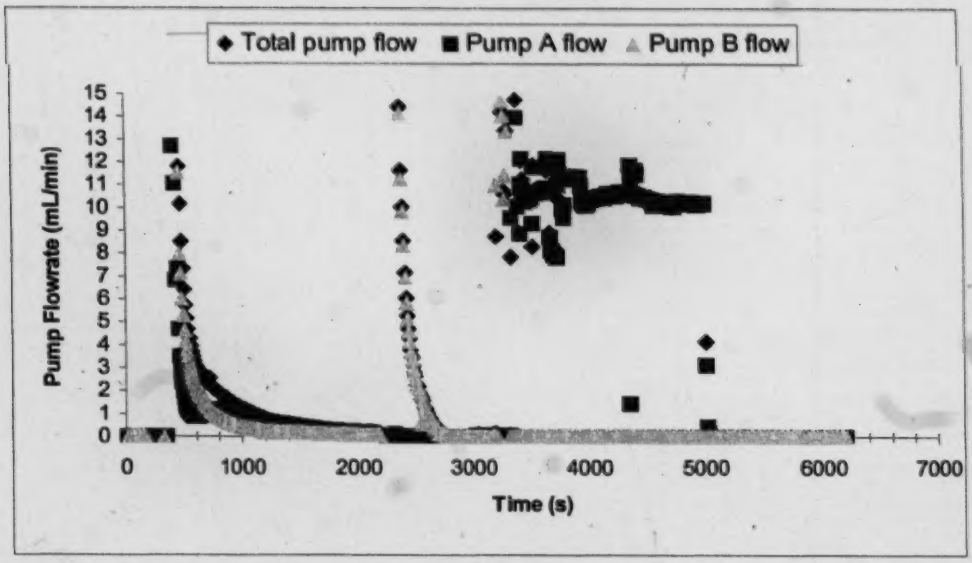


Figure 4.4: Pump flow data for single-cycle (2002-06-18) extraction (reduced scale)

Sample flow rate data for a double cycle extraction is shown on a large scale in Figure 4.5, and on a reduced scale in Figure 4.6.

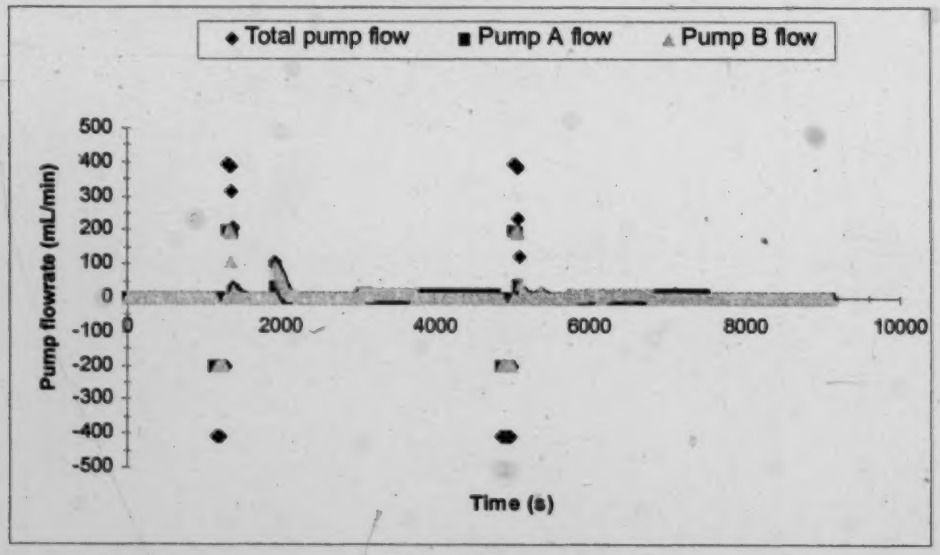


Figure 4.5: Pump flow data for double cycle (2002-08-19) extraction (large scale)

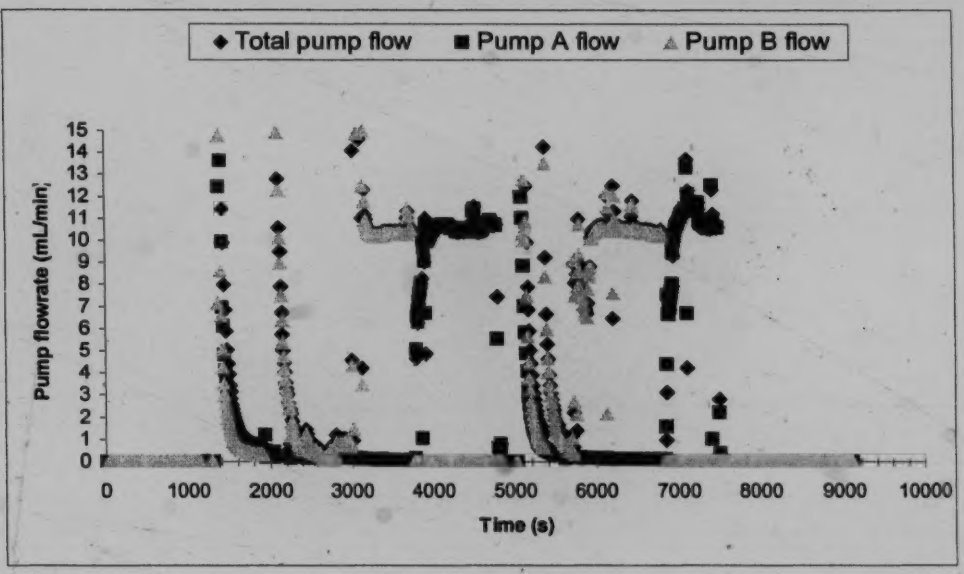


Figure 4.6: Pump flow data for double cycle (2002-08-19) extraction (reduced scale)

Flow rate data were collected from the ISCO pumps, which measures the carbon dioxide flow rate from the pumps at the experimental pressure.

Figure 4.3 shows that the maximum flow rate into each pump when refilling from the CO_2 cylinder is around -200 mL/min, and the maximum flow rate out of the pumps when filling up the vessel is around +200 mL/min. These values agree with the maximum flow rate setting on the pump controller, set at –204 mL/min for refilling from the cylinder, or +204 mL/min when delivering from the pumps. The combined flow of the two pumps A and B, called Total Pump Flow, could therefore be +400 mL/min or –400 mL/min, or half of these values when only one pump is in operation. This pattern is repeated twice in the case of the double cycle extraction (see Figure 4.5), as the pumps had to be refilled and re-pressurized at about 5000 s.

The desired total flow rate from the pumps is 10 mL/min during the dynamic extraction. Examination of the flow pattern on a reduced scale for the single cycle experiment (Figure 4.4) shows the total pump flow is approximately the desired 10 mL/min from 3200 s to 5000 s, which is the duration of the dynamic extraction. Figure 4.4 also indicates an initial instability in the total pump flow experienced around 3200 s. This instability was the result of the manual fine-tuning of the metering valve to obtain the desired total flow rate.

For the reduced scale data for double cycle experiments shown in Figure 4.6, this pattern of initial fine-tuning and stabilization of flow around 10 mL/min is also experienced at around 3000 s for the first dynamic extraction, and repeated at around 5500 s for the second dynamic extraction. During the first dynamic extraction (from around 3000 s to 4800 s), the initially running pump B ran out of CO_2 and stopped at around 4000 s, while pump A maintained flow afterwards until 4500 s – the end of the first dynamic extraction. Also, for the second dynamic extraction (from around 5700 to 7500 s), the initially running pump B ran out of CO_2 and stopped at around 6800 s, and pump A continued and maintained flow until the end of the experiment at 7500 s.

4.1.3 Temperature Data

The extraction temperature inside the vessel was monitored using the thermistor probe inserted into the vessel. Figure 4.7 and Figure 4.8 show the temperature data collected during single cycle and double cycle extractions, respectively. Visual monitoring and control of the water bath temperature was achieved with a mercury

thermometer placed in the water bath. The water bath temperature was stabilized at ±0.5°C of the desired temperature by adding ice cubes to bath during rising temperatures, or by increasing the heating during falling temperatures. Since the bath temperature was typically the same as that in the vessel, as measured by the thermistor, direct control of the vessel extraction temperature is therefore established by adequate control of bath temperature.

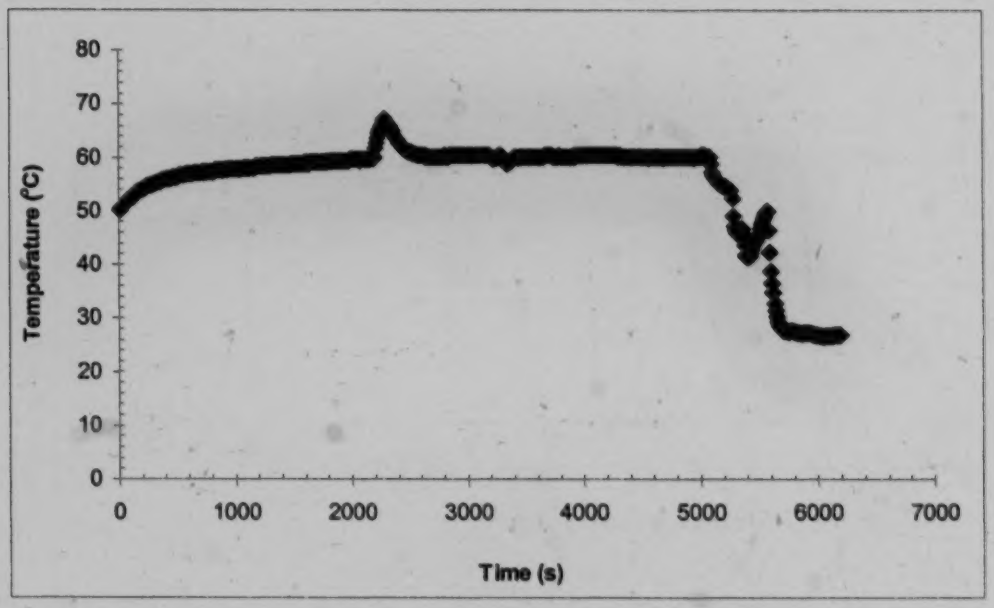


Figure 4.7: Sample temperature data for single cycle (2002-06-18) extraction

In Figure 4.7, the vessel temperature gradually increased and stabilized at 60°C. When the high pressure CO_2 was introduced to the vessel at 2200 s, the temperature then immediately increased to around 67°C before gradually decreasing back to 60°C. During this same time period, the water bath temperature was monitored and found to remain

stable at 60°C. This phenomenon was also experienced by Savoie (2002), and can be explained by the sudden increase in pressure in the vessel. Assuming the fluid behaves as an ideal gas, increasing the pressure in the constant volume extraction vessel causes an increase in the temperature of the system. The vessel temperature drops back to the circulating water temperature as the gained heat becomes lost to the environment. This same phenomenon was also experienced for the double cycle extraction experiments, a sample of which is shown in Figure 4.8.

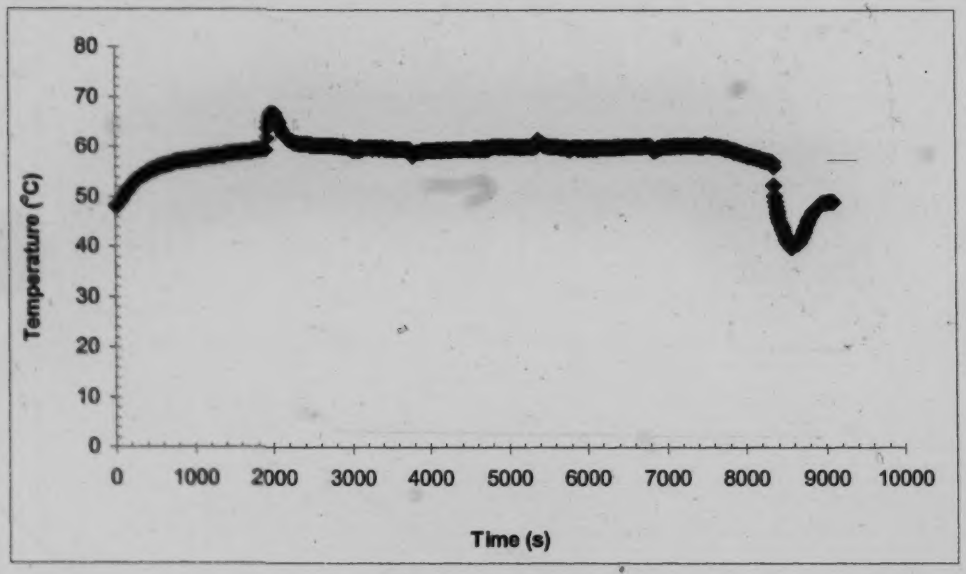


Figure 4.8: Sample temperature data for double cycle extraction (2002-08-19)

Although the water bath provided consistently stable heating and good temperature control for this work, temperatures higher that 60°C could not be investigated as the circulation heater could not sufficiently heat the volume of water in the bath to temperatures above 60°C. The use of a vessel with a heating jacket, rather than

vessel immersed in water bath, would allow the achievement of higher temperatures. Water or alternative heated fluids (oil for higher temperatures) could be used. The heating jacket and various fluids would facilitate the investigation of extractions at higher temperatures.

4.1.4 Visual Observations

4.1.4.1 Observation of the cuttings before and after SC CO_2 extraction

As an indication of the extraction efficiency, visual observations of the drill cuttings were made prior to and following extraction. Figure 4.9 provides a visual representation of the drill cuttings before and after extraction. In the vial shown on the left of Figure 4.9, the raw cuttings prior to extraction by SC CO_2 appeared extremely viscous, wet and dark in color. Once the SC CO_2 extraction was completed, the cuttings appeared dry, grainy, free flowing and much lighter in color (Figure 4.9, right vial). The oil extracted from the drill cuttings was visible in the glass wool traps, which turned yellow, the same color as the diesel oil used to prepare the OBMs. This oil also had the characteristic diesel oil smell.

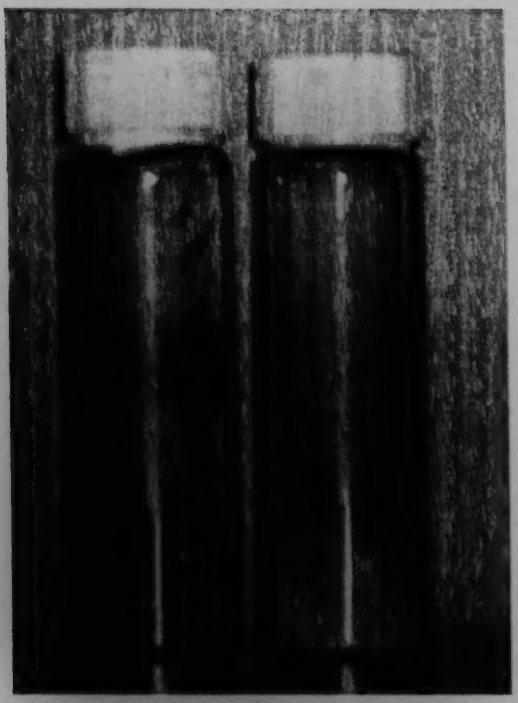


Figure 4.9: OBM drill cuttings before and after extraction

4.1.4.2 Observations of cuttings in the extraction vessel

Mixing was provided during the extraction experiment using a magnetic stir bar placed inside the vessel with the cuttings. It should be noted that due to the viscous nature of the raw drill cuttings prior to extraction, the magnetic stir bar was not able to mix the cuttings under ambient conditions of temperature and pressure. However, visual observations of the cuttings inside the vessel after extraction indicated that the magnetic stir bar was able to mix the raw cuttings under supercritical conditions. A mixing pattern created by the stir bar was observed in the cuttings after extraction, suggesting that the

cuttings' fluid properties may have been enhanced under supercritical conditions, thus making some mixing by the stir bar possible.

4.2 PETROLEUM HYDROCARBON ANALYSES

Cuttings samples were analyzed for petroleum hydrocarbon content (C_{11} to C_{32}) before and after the extraction experiments using gas chromatography/flame ionization detection (GC/FID). Using these measurements, it was possible to calculate the extraction efficiencies and determine how much hydrocarbon was extracted from the cuttings.

Pure diesel oil, oil from raw drill cuttings, and oil from SC CO_2-extracted drill cuttings were also analyzed by gas chromatography to establish the difference, if any, between the oil extracted by SC CO_2, oil in raw unextracted oil-contaminated cuttings, and pure diesel oil obtained from the drilling site.

4.2.1 Alkane Retention Time

Figure 4.10 shows the chromatogram of the 2000ppm Decane (C_{10}), hexadecane (C_{16}) and dotriacontane (C_{32}) standards respectively. The retention time of these alkanes was determined from these chromatograms. These retention times are provided in Table 4.1, which are averages of several retention time runs for each alkane.

Figure 4.10: C_{10}, C_{16} and C_{32} retention time chromatogram

Table 4.1: Retention time determination

Peak	Retention time (min)
Methylene Chloride (solvent)	2.6
C_{10}	8.4
C_{16}	15.2
C_{32}	29.4

The C_{10}-C_{32} retention time window is therefore defined as being from 8.4 and 29.4 minutes.

4.2.2 GC/FID Calibration

Figure 4.11 shows the chromatogram for the methylene chloride blank, and a 15,000 ppm diesel standard. For peak area integration for the C_{10} to C_{32} petroleum hydrocarbons, a horizontal baseline had to be drawn. This horizontal baseline was drawn using the Horizontal Minimum (HM) function of the Star Chromatography software, and is as shown in Figure 4.12, projected along the entire chromatogram.

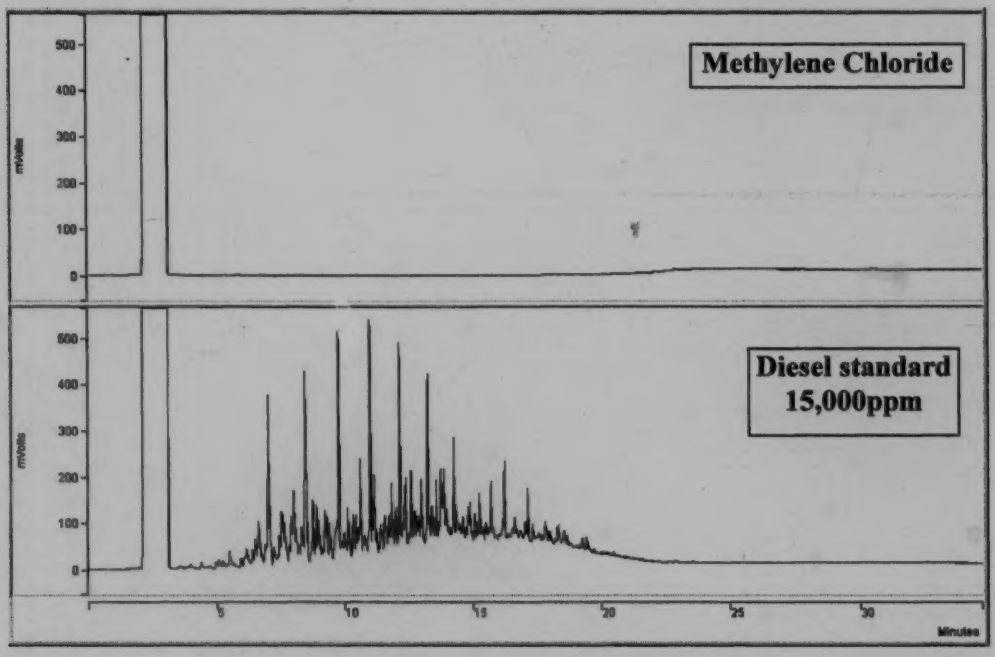


Figure 4.11: Chromatogram of Methylene Chloride blank and diesel standard

Once the horizontal baseline has been drawn, the peak area from 8.4 and 29.4 minutes is integrated, and the area summed using the GR (Group Peaks) function of the Star Chromatography data handling software. This feature allows all peaks in this retention window to be reported as a single peak with the separation code GR and a retention time set to the midpoint of the window (see Appendix B1). This summed-up area is then reported as the Chromatogram Area for the particular standard, sample or solvent blank injection.

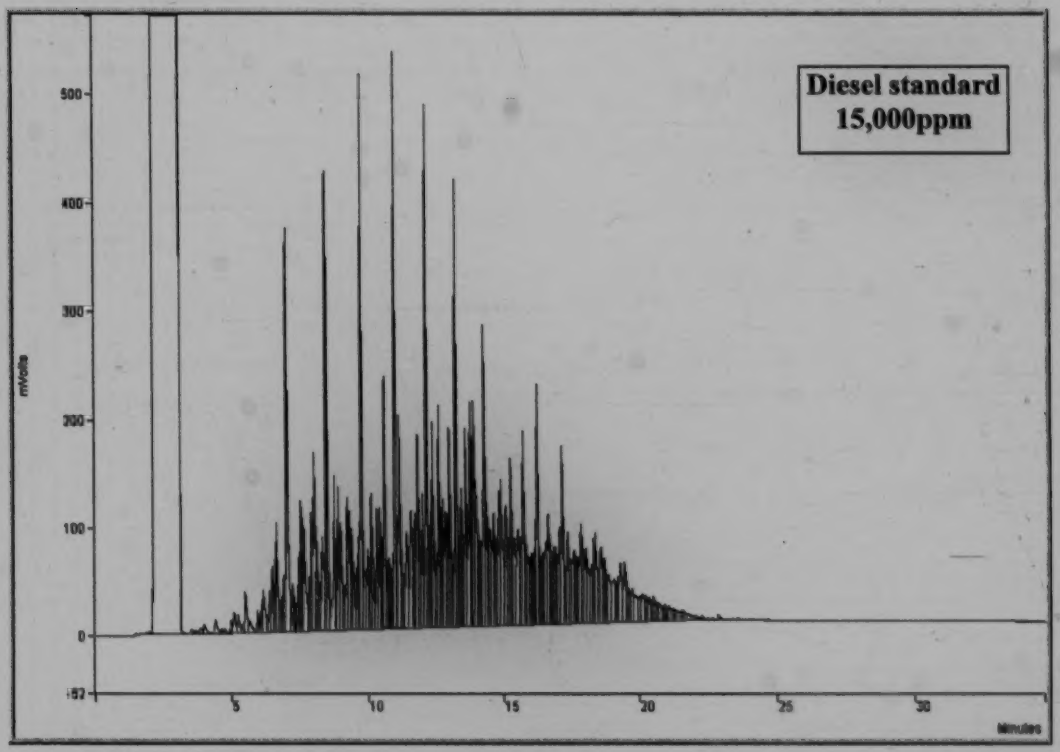


Figure 4.12: Chromatogram baseline projected between C_{10} and C_{32} retention time (large scale)

For each batch of standards or samples injected into the GC, the chromatogram area of the methylene chloride blank is subtracted from that of the standard or sample to compensate for column bleed. This compensation therefore gives the Corrected Chromatogram Area for the standard or sample. This corrected chromatogram area of the standards was plotted against the diesel standards' concentration to give the six-point calibration curve, shown in Figure 4.13 (detailed calculations are given in Appendix B2)

This calibration gave a very good fit, with a linear correlation coefficient of 0.9994, clearly better than the minimum 0.99 required for quantitative purposes (USEPA 1996d). With a minimum calibration standard of 150 ppm, and the method as outlined in Chapter 3, the method detection limit (MDL) for the analyses is 0.10% cuttings petroleum hydrocarbon content (i.e. 1000 mg of hydrocarbon / kg of cuttings).

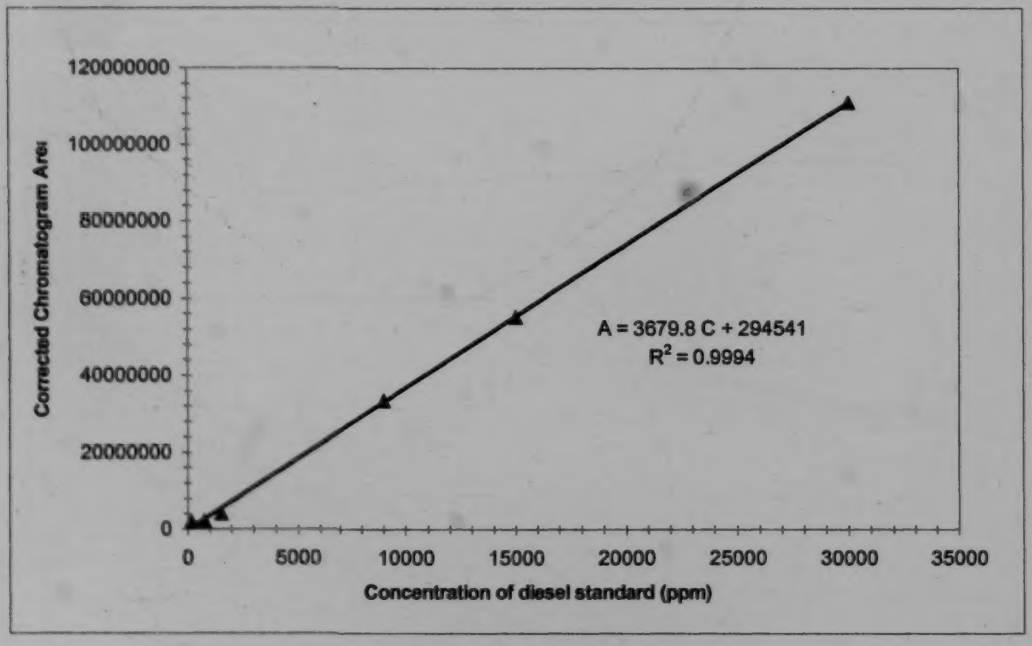


Figure 4.13: GC/FID diesel standards calibration curve

4.2.3 Sample Analyses

To examine the variability in results due to GC injections, sampling and SFE extractions, the results for the double cycle extractions at 12.4MPa and 60°C is presented in Table 4.2. Table 4.3 shows the petroleum hydrocarbon content analyses for raw SFE-untreated drill cuttings and SFE-extracted cuttings at all extraction conditions. A sample chromatogram and resulting output is presented in Appendix B1, while a sample cuttings' petroleum hydrocarbon content calculation also presented in Appendix B4.

4.2.3.1 Variability in results

Table 4.2 shows that the relative standard deviations (i.e. ratio of standard deviation to mean, expressed in percentage) ranged from 3% to 63%. It is believed that the high standard deviations, compared to the obtained means, may be due to factors such as sample heterogeneity, inadequate mixing and other uncontrollable operational variables during SFE extraction, variability in extracted cuttings sampling, and GC analyses.

To investigate these variabilities, the results of double cycle extractions at 12.4 MPa and 60°C carried out on two different days are presented in Table 4.2. Recall that for a particular SFE extraction, three subsamples of the SFE-extracted cuttings were prepared for GC analyses. Ideally, triplicate GC injections of all three subsamples of each of the duplicate SFE extractions at the same conditions should be carried out for all extraction conditions. This extent of sampling and analysis would have required extensive time,

resources, and GC injections without necessarily reducing the variability in the results. Selective GC injections were therefore done to reduce the total amount of GC injections required, while making sure that reliable results were still being generated. The results presented in Table 4.2 for the double-cycle extraction at 12.4 MPa and 60°C were therefore those obtained from using data from all individual analyses shown in Table 4.2 (that is, from the last three columns in Table 4.2). Also, all the other values reported in Table 4.3 were also obtained using data from individual analyses done at the particular extraction conditions. Appendix B5 presents the individual data set from which the results presented in Table 4.3 were obtained.

Table 4.2 shows that, apart from the effect of the 0.03% petroleum hydrocarbon content determined from the second GC injection of the second subsample of the August 20 extraction, the relative standard deviation of most GC injections and between cuttings' subsamples were generally below 27% (see Table 4.2). In order to identify which factors (i.e. SFE extraction, cuttings subsample, GC analyses) considerably increased the variability in the results, analysis of variance (ANOVA) calculations were performed at a 90% confidence level.

The ANOVA analysis of the data shown in Table 4.2 (see Appendix C1) suggests that while there is a difference between the mean hydrocarbon content of cuttings' subsamples analyzed for the extraction performed on 20-August, there was no difference between the mean hydrocarbon content of cuttings' subsamples analyzed for the extraction performed on 19-August. These two ANOVA analyses suggest that cuttings hydrocarbon content determination may or may not differ from one subsample batch to another, for the same SC CO_2 extraction batch. This trend also seems to be dependent on

the particular SC CO_2 extraction. In fact, a difference was detected in the mean of hydrocarbon content results obtained for the 20-August and 19-August SC CO_2 extractions at the same conditions (single cycle, 12.4MPa, 60°C extractions) (Appendix C2). This trend suggests that the SFE extracted cuttings' hydrocarbon content results may be different from one SC CO2 extraction to another. This variability may be due in part to the heterogeneity in cuttings subsample used for the SC CO_2 extractions, and SC CO_2-extraction operational variables (e.g. mixing), which could not be adequately controlled in this work.

In Table 4.3, the mean petroleum hydrocarbon content for SFE extracted cuttings showed relative standard deviations of up to 63%. Extraction efficiencies obtained for single cycle extractions at 8.3 MPa and 35°C, at 10.3 MPa and 35°C, and at 10.3 MPa and 50°C were less than those obtained at other extraction conditions, which ranged from 83% to 90% (i.e. mean cuttings hydrocarbon content ranging from 2.94 to 1.76%). The difference of these obtained cuttings' hydrocarbon content had to be tested through an ANOVA test. This is more so since high relative standard deviations were obtained in the results, as shown in Table 4.3. The ANOVA analysis of the mean cuttings petroleum hydrocarbon content for extractions between 12.4 and 17.2 MPa is presented in Appendix C3, and indicates that there is a difference between the means for the groups of extraction conditions.